Synthesis and Crystal Structure of [guanidinium][Ni(dmit)$_2$]$_2$ and [1,1-dimethylguanidinium][Ni(dmit)$_2$]$_2$ (dmit = 2-Thioxo-1,3-dithiole-4,5-dithiolate). Intermolecular Orbital Integral Overlap Calculations and Electrical Conductivities

Yvonne S. J. Veldhuizen,[1a] Nora Veldman,[1b] Anthony L. Spek,*,[1b] Christophe Faulmann,[1c] Jaap G. Haasnoot,*,[1a] and Jan Reedijk[1a]

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex, France

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Electro-oxidation of a solution of [NBu$_4$][Ni(dmit)$_2$] (dmit = $C_3S_5^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate) in the presence of a large excess of guanidinium tetrafluoroborate (GuaBF$_4$) or 1,1-dimethylguanidinium tetrafluoroborate (Me$_2$GuaBF$_4$) yields black crystals of [Gua][Ni(dmit)$_2$]$_2$ (**1**) and [Me$_2$Gua][Ni(dmit)$_2$]$_2$ (**2**), respectively. The molecular structures of **1** and **2** have been determined by X-ray crystallography. Crystal data for **1**: triclinic, space group $P\bar{1}$ (No. 2) with a = 6.472(3) Å, b = 7.420(4) Å, c = 33.468(5) Å, α = 87.97(3)°, β = 85.80(3)°, γ = 70.96(4)°, V = 1515.1(12) Å^3, and Z = 2. Crystal data for **2**: triclinic, space group $P\bar{1}$ (No. 2) with a = 8.9864(12) Å, b = 10.0138(9) Å, c = 18.238(2) Å, α = 81.963(9)°, β = 89.071(10)°, γ = 72.447(9)°, V = 1548.8(3) Å^3, and Z = 2. In compound **1** two crystallographically independent Ni(dmit)$_2$ units, Ni(1)(dmit)$_2$ and Ni(2)(dmit)$_2$, are lying in a head-to-tail orientation forming two different sheets of units in the *ab* plane. In the Ni(1)(dmit)$_2$ sheet the units are slightly dimerized and a *two*-dimensional network of short S···S contacts is formed. The Ni(2)(dmit)$_2$ sheet shows no dimerization, and a *one*-dimensional network can be seen. The sheets are connected along the *c*-axis via short S···S contacts of the thione sulfur atoms and via N–H···S hydrogen bonds with the cations which are lying in between. In compound **2** two crystallographically independent Ni(dmit)$_2$ units are lying in a face-to-face orientation thereby forming one type of anionic sheet in the *ab* plane. A two-dimensional network of short S···S contacts is formed by slightly dimerized Ni(dmit)$_2$ units in the sheet. Intersheet contacts are present through short S···S contacts and N–H···S hydrogen bonds as in compound **1**. For both compounds intermolecular orbital overlap integral calculations point toward a weak two-dimensional conduction pathway in the *ab* plane. Conductivity measurements indicate a room temperature value of 32 S·cm^{-1} for **1** and 0.15 S·cm^{-1} for **2**. Both compounds behave as semiconductors in the temperature range of 300–100 K with E_a = 0.12 and 0.13 eV for **1** and **2**, respectively.

Introduction

In 1986 the discovery of the superconducting properties of [TTF][Ni(dmit)$_2$]$_2$ (TTF = tetrathiafulvalene, dmit = $C_3S_5^{2-}$ = 2-thioxo-1,3-dithiole-2-thione-4,5-dithiolate), the first formally inorganic molecular superconductor,[2] initiated intensive research in the area of conducting coordination compounds based on dmit. A rich variety of combinations of [cation]$_x$[M(dmit)$_2$] (M = Ni, Pd, Pt; $0 < x < 1$) have been synthesized, most of them being semiconductors but some of them exhibiting metallic conductivity around room temperature. In 1991 and 1992 two extensive reviews appeared on the subject of dmit compounds.[3,4] So far a total of six dmit compounds show superconducting properties, albeit at low temperature and until recently only at high pressure.[2,5–9] However, in 1993 the first ambient pressure Ni(dmit)$_2$ superconductor, i.e. α-EDT-TTF-[Ni(dmit)$_2$], was published.[10]

Generally, the conduction path in the Ni(dmit)$_2$ salts is formed through overlapping orbitals of the sulfur atoms in the ligands. The idea to improve this conduction path by replacing one or more of the sulfur atoms by the larger selenium has already yielded several partially oxidized M(C$_3$S$_{5-x}$Se$_x$)$_2$ (M = Ni, Pd) compounds.[11] It was found that the structural and/or electronic properties of these compounds can be quite different from those of the corresponding dmit salts.

The cations used in the Ni(dmit)$_2$ salts are open- as well as closed-shell cations. By using an open-shell cation like TTF, an extra conduction path is introduced by the sulfur atoms on the periphery of this molecule. However, a superconductor such as [NMe$_4$][Ni(dmit)$_2$]$_2$,[5] in which NMe$_4^+$ is a closed-shell (or

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* To whom correspondence should be addressed: A.L.S., crystallographic matters; J.G.H., all other matters.

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(1) (a) Leiden Institute of Chemistry, Leiden University. (b) Utrecht University. (c) Laboratoire de Chimie de Coordination du CNRS, Toulouse, France.

(2) Brossard, L.; Ribault, M.; Bousseau, M.; Valade, L.; Cassoux, P. *C. R. Acad. Sc. Paris, Ser. 2* **1986**, *302*, 205.

(3) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, *110*, 115.

(4) Olk, R.-M.; Olk, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *117*, 99.

(5) Kobayashi, A.; Kim, H.; Sasaki, Y.; Kato, R.; Kobayashi, H.; Moriyama, S.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1987**, 1819.

(6) Brossard, L.; Hurdequint, H.; Ribault, M.; Valade, L.; Legros, J.-P.; Cassoux, P. *Synth. Met.* **1988**, *27*, B157.

(7) Brossard, L.; Ribault, M.; Valade, L.; Cassoux, P. *J. Phys. Fr.* **1989**, *50*, 1521.

(8) Kobayashi, A.; Kobayashi, H.; Miyamoto, A.; Kato, R.; Clark, R. A.; Underhill, A. E. *Chem. Lett.* **1991**, 2163.

(9) Kobayashi, H.; Bun, K.; Naito, T.; Kato, R.; Kobayashi, A. *Chem. Lett.* **1992**, 1909.

(10) Tajima, H.; Inokuchi, M.; Kobayashi A.; Ohta, T.; Kato, R.; Kobayashi, H.; Kuroda, H. *Chem. Lett.* **1993**, 1235.

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"spectator") cation, proves that this is not a general requirement for the occurrence of superconductivity in dmit salts. The size and shape of the cation determine the final crystal structure and—as a consequence—the electronic properties of the compound. So far very little is known about why a certain cation forms a certain crystal structure with M(dmit)$_2$ anions. Small changes may have major consequences. For example changing NMe_4^+ for $NEtMe_3^+$ [12] in [cation][Ni(dmit)$_2$]$_2$ results in a significantly different crystal structure and transforms the salt from a superconductor to a semiconductor.

Closed-shell cations used up to now are mostly of the tetraalkylammonium type, including the divalent cation 2,2,7,7-tetramethyl-2,7-diazoniaoctane.[13] A few compounds using small saturated and unsaturated ring systems, like *N,N*-dimethylpyrrolidinium and 1,2,3-trimethylimidazolium have also been synthesized.[14,15] In the present study the first Ni(dmit)$_2$ compound in combination with a planar closed-shell cation, guanidinium ($C(NH_2)_3^+$, abbreviated by Gua), is described. In many Ni(dmit)$_2$ compounds the cations crystallize between separated sheets of Ni(dmit)$_2$ units. A planar cation might crystallize with its plane parallel to these sheets, so that the distance between the sheets will become short. This may result in an increased overlap of sulfur orbitals between the sheets which introduces an extra dimension in the conductivity of the compound.

Guanidinium is also an interesting cation because of its possibility to form hydrogen bonds with sulfur atoms of dmit. It is known that in the organic superconducting salts *β*-(ET)$_2$X (ET = bis(ethylenedithio)tetrathiafulvalene and $X^- = IBr_2^-$, AuI_2^-, I_3^-) intermolecular hydrogen···hydrogen and hydrogen···anion contacts play an important role in the determination of the lattice softness with respect to the translational and/or librational modes of vibration. These phonons are related to the occurrence of superconductivity in these salts.[16,17] Although N–H···S hydrogen bonds are often not very strong,[18] they certainly will have an influence on the lattice structure and softness and—consequently—on the properties of a compound.

Table 1. Crystallographic Data for [Gua][Ni(dmit)$_2$]$_2$ (**1**) and [Me$_2$Gua][Ni(dmit)$_2$]$_2$ (**2**)

	1	2
empirical formula	$C_{13}H_6N_3Ni_2S_{20}$	$C_{15}H_{10}N_3Ni_2S_{20}$
fw	962.92	990.97
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cryst system	triclinic	triclinic
a, Å	6.472(3)	8.9864(12)
b, Å	7.420(4)	10.0138(9)
c, Å	33.468(5)	18.238(2)
α, deg	87.97(3)	81.963(9)
β, deg	85.80(3)	89.071(10)
γ, deg	70.96(4)	72.447(9)
V, Å^3	1515.1(12)	1548.8(3)
Z	2	2
D_{calcd}, g·cm^{-3}	2.111(2)	2.1248(4)
D_{obs}, g·cm^{-3}	2.09	2.10
μ_{calcd}, cm^{-1}	144.7	25.4
T, K	295	150
radiation; λ, Å	Cu Kα; 1.541 84	Mo Kα; 0.710 73
R^a	0.0924	0.0532
$R_w{}^b$/w$R2^c$	0.1296	0.1271

$^aR = \sum||F_o| - |F_c||/\sum|F_o|$. $^bR_w = [\sum[w(||F_o| - |F_c||)^2]/\sum[w(F_o{}^2)]]^{1/2}$. ^{c}w$R2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.

In this paper we also describe the influence of the substitution of two hydrogen atoms by methyl groups, i.e., the combination of 1,1-dimethylguanidinium (Me$_2$Gua) with Ni(dmit)$_2$.

Experimental Section

Synthesis of Guanidinium Tetrafluoroborate. A 0.01 mol amount of guanidinium carbonate (Aldrich) was suspended in 25 mL of ethanol. A small excess of tetrafluoroboric acid (~54% in diethyl ether) was added dropwise until pH = 3–4. The product dissolved, and the remaining solid was removed by filtration. The solvent was evaporated, and the product was crystallized by slow evaporation of a solution of the salt in a mixture of acetone and ethyl acetate. Infrared spectroscopy shows that carbonate is replaced by tetrafluoroborate. The salt was used without further purification.

Synthesis of 1,1-Dimethylguanidinium Tetrafluoroborate. A 5 mmol amount of barium hydroxide octahydrate was added to a solution of 5 mmol of 1,1-dimethylguanidinium sulfate (Aldrich) in 30 mL of water. The precipitated barium sulfate was filtered off, and a small excess of tetrafluoroboric acid (~54% in diethyl ether) was added dropwise to the filtrate until pH = 3–4. The solvent was evaporated and the residue was dissolved in a minimum amount of ethanol pa. The product crystallized after subsequent addition of a few milliliters of diethyl ether at −15 °C. Infrared spectroscopy shows that sulfate is replaced by tetrafluoroborate. The salt was used without further purification.

Synthesis of [Gua][Ni(dmit)$_2$]$_2$ (1) and [Me$_2$Gua][Ni(dmit)$_2$]$_2$ (2). It appeared to be difficult to obtain the [cation][Ni(dmit)$_2$] compounds as pure starting materials for electro-oxidation. Therefore electro-oxidation was carried out by the so-called "large excess method". Under a dinitrogen atmosphere a solution of 0.05 mmol of [NBu$_4$][Ni(dmit)$_2$], prepared by the general method of Steimecke et al.,[19] and 0.7 mmol of (cation)BF$_4$ in 30 mL anhydrous acetonitrile was poured into a H-tube equipped with a fine porosity frit and two platinum wires (∅ = 0.8 mm). A constant current of approximately 1.2 μA was applied, and after 1 week black crystals could be isolated from the anode.

In an alternative oxidation [Gua][Ni(dmit)$_2$]$_2$ (**1**) was obtained by using dioxygen from the air. A flask containing the same solution as for electro-oxidation was exposed to air during 2 weeks. Crystals with the same cell dimensions as **1** were collected.

Elemental analyses, performed by Groningen University, were in agreement with the molecular formulas $C_{13}H_6N_3Ni_2S_{20}$ (**1**) and $C_{15}H_{10}N_3Ni_2S_{20}$ (**2**; C, H, N only).

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(11) (a) Beno, M. A.; Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M. *The Physics and Chemistry of Organic Superconductors*; Saito, G., Kagoshima, S., Eds.; Springer Verlag: Berlin, 1990; p 369. (b) Kini, A. M.; Beno, M. A.; Budz, S.; Wang, H. H.; Williams, J. M. *Materials Research Society Symp. Proc.* **1990**, *173*, 177. (c) Cornelissen, J. P.; Reefman, D.; Haasnoot, J. G.; Spek, A. L.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 345. (d) Cornelissen, J. P.; Haasnoot, J. G.; Reedijk, J.; Faulmann, C.; Legros, J.-P.; Cassoux, P.; Nigrey, P. J. *Inorg. Chim. Acta* **1992**, *202*, 131. (e) Cornelissen, J. P.; Pomarède, B.; Spek, A. L.; Reefman, D.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1993**, *32*, 3720. (f) Faulmann, C.; Legros, J.-P.; Cassoux, P.; Cornelissen, J. P.; Haasnoot, J. G.; Reedijk, J. *Synth. Met.* **1993**, *55–57*, 2063. (g) Faulmann, C.; Legros, J.-P.; Cassoux, P.; Cornelissen, J. P.; Brossard, L.; Inokuchi, M.; Tajima, H.; Tokumoto, M. *J. Chem. Soc., Dalton Trans.* **1994**, 249.

(12) Kato, R.; Kobayashi, H.; Kim, H.; Kobayashi, A.; Sasaki, Y.; Mori, T.; Inokuchi, H. *Synth. Met.* **1988**, *27*, B359.

(13) Cornelissen, J. P.; Müller, E.; Vaassens, P. H. S.; Haasnoot, J. G.; Reedijk, J.; Cassoux, P. *Inorg. Chem.* **1992**, *31*, 2241.

(14) (a) Cornelissen, J. P.; Haasnoot, J. G.; Le Loux, R.; Reedijk, J. *Synth. Met.* **1991**, *42*, 2315. (b) Kobayashi, H.; Kato, R.; Kobayashi, A. *Synth. Met.* **1991**, *42*, 2495. (c) Cornelissen, J. P.; Le Loux, R.; Jansen, J.; Haasnoot, J. G.; Reedijk, J.; Horn, E.; Spek, A. L.; Pomarède, B.; Legros, J.-P.; Reefman, D. *J. Chem. Soc., Dalton Trans.* **1992**, 2911.

(15) (a) Reefman, D.; Cornelissen, J. P.; Haasnoot, J. G.; De Graaff, R. A. G.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 3933. (b) Cornelissen, J. P.; Creyghton, E. J.; De Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chim. Acta* **1991**, *185*, 97.

(16) Whangbo, M.-H.; Williams, J. M.; Schultz, A. J.; Emge, T. J.; Beno, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 90.

(17) Williams, J. M.; Wang, H. H.; Emge, T. J.; Geiser, U.; Beno, M. A.; Leung, P. C. W.; Carlson, K. D.; Thorn, R. J.; Schultz, A. J. *Prog. Inorg. Chem.* **1987**, *35*, 51.

(18) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids: Methods of Molecular Structure Determinations*; W. A. Benjamin, Inc.: New York, 1968.

(19) Steimecke, G.; Sieler, H. J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49.

Table 2. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for $[\mathrm{Gua}][\mathrm{Ni(dmit)_2}]_2$ (Esd's in Parentheses)

atom	*x*	*y*	*z*	U(eq),[a] Å^2
Ni(1)	0.2925(5)	0.7092(4)	0.02228(8)	0.0252(8)
S(1)	−0.0207(9)	1.0161(8)	−0.1737(14)	0.0462(16)
S(2)	0.2996(8)	0.9453(6)	−0.11098(12)	0.0312(11)
S(3)	−0.1110(8)	0.8698(7)	−0.09350(13)	0.0336(14)
S(4)	0.4474(7)	0.8156(6)	−0.02847(12)	0.0300(11)
S(5)	0.0077(7)	0.7318(6)	−0.00987(12)	0.0306(13)
S(6)	0.5713(7)	0.7008(6)	0.05503(12)	0.0287(11)
S(7)	0.1386(8)	0.5980(7)	0.07253(12)	0.0314(13)
S(8)	0.6827(8)	0.5726(7)	0.13996(13)	0.0343(16)
S(9)	0.2850(8)	0.4815(7)	0.15656(12)	0.0336(15)
S(10)	0.6002(9)	0.4252(7)	0.22031(13)	0.0409(16)
C(1)	0.055(3)	0.945(2)	−0.1281(5)	0.032(5)
C(2)	0.259(3)	0.856(2)	−0.0637(4)	0.025(5)
C(3)	0.067(3)	0.817(2)	−0.0545(4)	0.022(4)
C(4)	0.509(3)	0.610(2)	0.1010(5)	0.024(5)
C(5)	0.330(3)	0.570(2)	0.1078(5)	0.033(5)
C(6)	0.516(3)	0.492(2)	0.1743(5)	0.032(5)
Ni(2)	0.0418(5)	0.7347(4)	0.48731(8)	0.0298(9)
S(11)	−0.0922(10)	0.5956(8)	0.28327(15)	0.0492(18)
S(12)	−0.2759(8)	0.6877(7)	0.36643(14)	0.0397(16)
S(13)	0.1893(8)	0.6027(7)	0.34886(13)	0.0366(16)
S(14)	−0.2395(8)	0.7502(7)	0.45434(13)	0.0374(16)
S(15)	0.2662(8)	0.6587(7)	0.43475(12)	0.0357(14)
S(16)	−0.1780(8)	0.8091(7)	0.54055(13)	0.0371(14)
S(17)	0.3237(8)	0.7208(7)	0.51879(12)	0.0376(15)
S(18)	−0.0860(8)	0.8588(7)	0.62642(13)	0.0374(16)
S(19)	0.3784(8)	0.7832(7)	0.60547(12)	0.0352(15)
S(20)	0.2152(9)	0.8650(8)	0.68961(14)	0.0455(16)
C(7)	−0.063(3)	0.628(2)	0.3314(6)	0.039(6)
C(8)	−0.124(3)	0.694(2)	0.4068(5)	0.030(5)
C(9)	0.099(3)	0.649(2)	0.3984(5)	0.032(5)
C(10)	−0.001(3)	0.810(2)	0.5763(5)	0.032(5)
C(11)	0.216(3)	0.770(2)	0.5665(5)	0.030(5)
C(12)	0.164(3)	0.841(2)	0.6425(5)	0.031(6)
N(1)	0.558(3)	0.945(3)	0.2270(5)	0.054(6)
N(2)	0.281(3)	0.859(2)	0.2614(5)	0.055(7)
N(3)	0.261(3)	1.174(2)	0.2559(6)	0.055(7)
C(13)	0.367(3)	0.990(3)	0.2479(6)	0.042(6)

[a] U(eq) = $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[\mathrm{Gua}][\mathrm{Ni(dmit)_2}]_2$ (Esd's in Parentheses)

Ni(1)−S(4)	2.165(5)	Ni(2)−S(16)	2.165(6)
Ni(1)−S(5)	2.159(6)	Ni(2)−S(17)	2.145(6)
Ni(1)−S(6)	2.162(6)	S(11)−C(7)	1.67(2)
Ni(1)−S(7)	2.167(5)	S(12)−C(7)	1.69(2)
S(1)−C(1)	1.658(17)	S(12)−C(8)	1.739(19)
S(2)−C(1)	1.72(2)	S(13)−C(7)	1.72(2)
S(2)−C(2)	1.729(14)	S(13)−C(9)	1.725(17)
S(3)−C(1)	1.723(19)	S(14)−C(8)	1.713(17)
S(3)−C(3)	1.753(17)	S(15)−C(9)	1.705(19)
S(4)−C(2)	1.707(18)	S(16)−C(10)	1.718(19)
S(5)−C(3)	1.669(15)	S(17)−C(11)	1.697(17)
S(6)−C(4)	1.731(17)	S(18)−C(10)	1.739(17)
S(7)−C(5)	1.732(19)	S(18)−C(12)	1.71(2)
S(8)−C(4)	1.740(19)	S(19)−C(11)	1.759(19)
S(8)−C(6)	1.742(19)	S(19)−C(12)	1.744(19)
S(9)−C(5)	1.777(17)	S(20)−C(12)	1.662(18)
S(9)−C(6)	1.67(2)	C(8)−C(9)	1.38(3)
S(10)−C(6)	1.675(17)	C(10)−C(11)	1.35(3)
C(2)−C(3)	1.38(3)	N(1)−C(13)	1.32(3)
C(4)−C(5)	1.29(3)	N(2)−C(13)	1.32(3)
Ni(2)−S(14)	2.167(6)	N(3)−C(13)	1.34(3)
Ni(2)−S(15)	2.164(5)		
S(4)−Ni(1)−S(5)	92.4(2)	S(8)−C(6)−S(9)	114.9(10)
S(4)−Ni(1)−S(6)	87.1(2)	S(8)−C(6)−S(10)	119.1(12)
S(4)−Ni(1)−S(7)	179.0(2)	S(9)−C(6)−S(10)	126.0(11)
S(5)−Ni(1)−S(6)	177.3(2)	S(14)−Ni(2)−S(15)	93.0(2)
S(5)−Ni(1)−S(7)	87.3(2)	S(14)−Ni(2)−S(16)	87.9(2)
S(6)−Ni(1)−S(7)	93.2(2)	S(14)−Ni(2)−S(17)	178.8(2)
C(1)−S(2)−C(2)	95.9(9)	S(15)−Ni(2)−S(16)	179.0(3)
C(1)−S(3)−C(3)	97.1(9)	S(15)−Ni(2)−S(17)	85.9(2)
Ni(1)−S(4)−C(2)	102.7(6)	S(16)−Ni(2)−S(17)	93.2(2)
Ni(1)−S(5)−C(3)	102.6(7)	C(7)−S(12)−C(8)	96.7(10)
Ni(1)−S(6)−C(4)	101.6(7)	C(7)−S(13)−C(9)	96.5(10)
Ni(1)−S(7)−C(5)	100.4(7)	Ni(2)−S(14)−C(8)	102.2(7)
C(4)−S(8)−C(6)	95.4(9)	Ni(2)−S(15)−C(9)	102.7(7)
C(5)−S(9)−C(6)	96.0(9)	Ni(2)−S(16)−C(10)	101.8(7)
S(1)−C(1)−S(2)	123.3(11)	Ni(2)−S(17)−C(11)	102.4(7)
S(1)−C(1)−S(3)	121.8(12)	C(10)−S(18)−C(12)	96.9(9)
S(2)−C(1)−S(3)	114.9(10)	C(11)−S(19)−C(12)	95.4(9)
S(2)−C(2)−S(4)	122.4(12)	S(11)−C(7)−S(12)	123.0(12)
S(2)−C(2)−C(3)	118.2(12)	S(11)−C(7)−S(13)	121.8(12)
S(4)−C(2)−C(3)	119.4(11)	S(12)−C(7)−S(13)	115.2(11)
S(3)−C(3)−S(5)	123.3(12)	S(12)−C(8)−S(14)	123.9(12)
S(3)−C(3)−C(2)	113.9(11)	S(12)−C(8)−C(9)	115.8(13)
S(5)−C(3)−C(2)	122.8(13)	S(14)−C(8)−C(9)	121.3(14)
S(6)−C(4)−S(8)	121.4(12)	S(13)−C(9)−S(15)	123.0(12)
S(6)−C(4)−C(5)	121.1(14)	S(13)−C(9)−C(8)	115.7(14)
S(8)−C(4)−C(5)	117.5(13)	S(15)−C(9)−C(8)	120.7(13)
S(7)−C(5)−S(9)	120.0(11)	S(16)−C(10)−S(18)	122.9(12)
S(7)−C(5)−C(4)	123.7(14)	S(16)−C(10)−C(11)	120.7(13)
S(9)−C(5)−C(4)	116.3(14)	S(18)−C(10)−C(11)	116.4(14)
S(17)−C(11)−S(19)	121.7(12)	S(19)−C(12)−S(20)	119.7(12)
S(17)−C(11)−C(10)	121.9(14)	N(1)−C(13)−N(2)	122(2)
S(19)−C(11)−C(10)	116.3(13)	N(1)−C(13)−N(3)	118(2)
S(18)−C(12)−S(19)	114.9(10)	N(2)−C(13)−N(3)	119.7(19)
S(18)−C(12)−S(20)	125.3(11)		

X-ray Crystallography

$[\mathrm{Gua}][\mathrm{Ni(dmit)_2}]_2$ (1). A black needle-shaped crystal (0.20 × 0.23 × 1.03 mm) inside a Lindemann glass capillary was transferred to an Enraf-Nonius CAD4-F sealed tube diffractometer (Zr filter, large homogeneous beam collimator). Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 18 well-centered reflections (SET4) in the range $15.1° < \theta < 27.0°$. The unit-cell parameters were checked for the presence of higher lattice symmetry.[20] Crystal data and details on data collection and refinement for **1** are given in Table 1. Data were collected in $\omega/2\theta$ mode with scan angle $\Delta\omega = 0.80 + 0.14 \tan\theta$. Intensity data of 6803 reflections were collected in the range $1.32° < \theta < 75.0°$, of which 6231 are independent. Data were corrected for *Lp* effects. The periodically measured reference reflection ($\bar{2}1\bar{5}$) showed no decay during 104.9 h of X-ray exposure time. Standard deviations of the intensities are based on counting statistics and were increased according to an analysis of the excess variance of the reference reflections:[21] $\sigma^2(I) = \sigma_{cs}^2(I) + (0.008I)^2$. The structure was solved by automated direct methods[22] (SIR-92). Refinement on F was carried out by full-matrix least-squares techniques[23] (SHELX76). Hydrogen atoms were included in the refinement on calculated positions (N−H = 0.90 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with one overall isotropic thermal parameter of 0.13(5) Å^2. An empirical absorption/extinction correction was applied (DIFABS,[24] correction range 0.718−2.365). Weights were introduced in the final refinement cycles. Convergence was reached at $R = 0.0924$, $R_w = 0.1296$, $w = 1/[\sigma^2(F) + 0.004515F^2]$, and $S = 4.38$ (variance), for 344 parameters and the 3167 reflections with $I > 2.5\sigma(I)$ used in the structure analysis. A final difference Fourier map showed

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(20) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

(21) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *A31*, 245.

(22) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(23) Sheldrick, G. M. SHELX76 Program for crystal structure determination. University of Cambridge, Cambridge, U.K., 1976.

(24) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

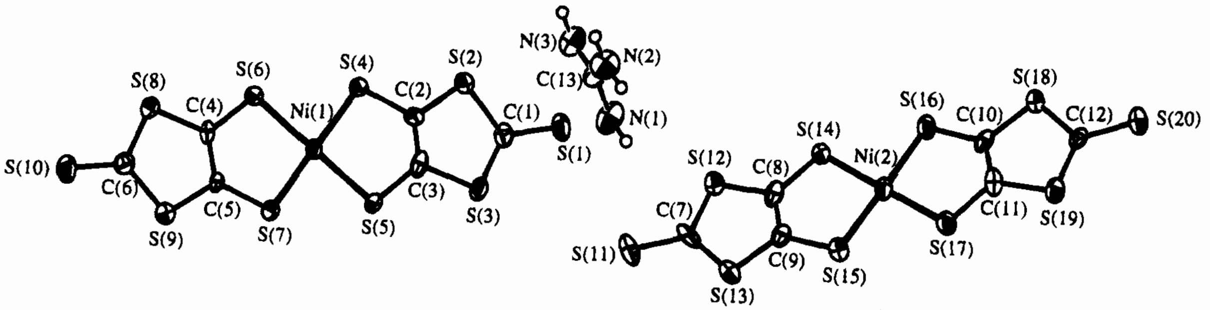
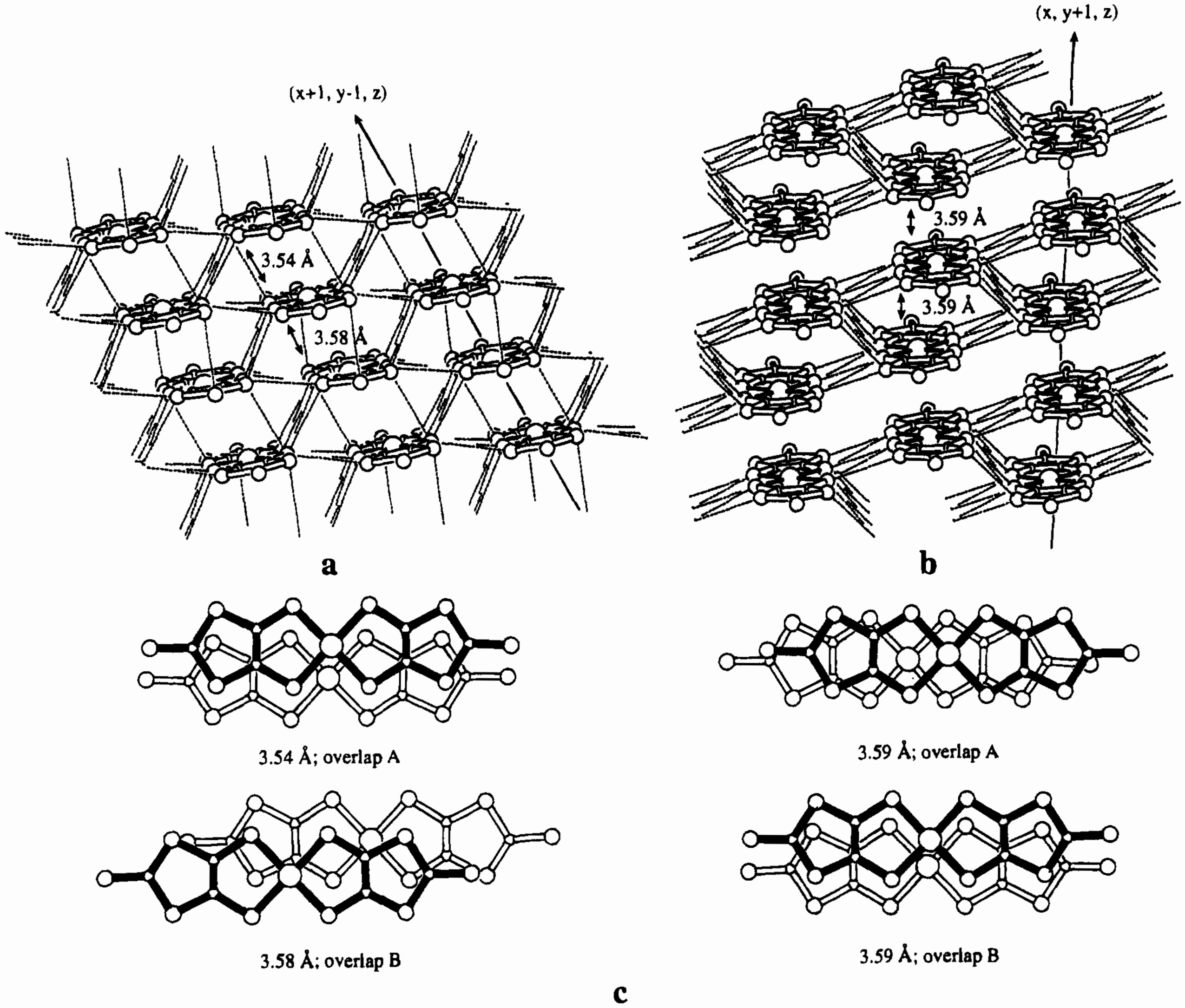


Figure 1. ORTEP 50% probability plot (PLATON[27]) of crystallographically independent units with atomic labeling scheme of [Gua][Ni(dmit)$_2$]$_2$.



a

b

3.54 Å; overlap A

3.59 Å; overlap A

3.58 Å; overlap B

3.59 Å; overlap B

c

Figure 2. Sheets of Ni(dmit)$_2$ units in the *ab* plane of [Gua][Ni(dmit)$_2$]$_2$: (a) Ni(1)(dmit)$_2$, (b) Ni(2)(dmit)$_2$, (c) modes of intermolecular overlapping of Ni(dmit)$_2$ units.

no residual density outside -1.64 and 1.40 e Å^{-3}. Neutral atom scattering factors were taken from Cromer and Mann;[25] anomalous dispersion corrections, from Cromer and Liberman.[26]

Geometrical calculations and ORTEP illustrations were done with PLATON.[27] All calculations were performed on a DECstation 5000 cluster. Positional parameters are listed in Table 2.

[Me$_2$Gua][Ni(dmit)$_2$]$_2$ (2). A thin plate-shaped black crystal (0.013 × 0.20 × 0.25 mm) was glued to the tip of a Lindemann glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T/rotating anode diffractometer. Accurate unit-cell parameters and an orientation matrix were determined of 25 well-centered reflections (SET4) in the range $10.0° < \theta < 15.6°$. The unit-cell parameters were checked for the presence of higher lattice symmetry.[20] Crystal data and details on data collection and refinement for **2** are given in Table 1. Data were collected at 150 K in the $\omega/2\theta$ mode with scan angle $\Delta\omega = 1.01 + 0.34 \tan \theta$. Intensity data of 10 022 reflections were collected in the range $2.2° < \theta < 27.5°$, of which 7102 are independent. Data were corrected for *Lp* effects and a linear decay of 10% as indicated by the reference reflections ($2\bar{2}\bar{3}$, $2\bar{2}0$, $40\bar{2}$). Standard deviations of the intensities are based on counting statistics. The structure was solved

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(25) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
(26) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(27) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

Table 4. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for $[Me_2Gua][Ni(dmit)_2]_2$ (Esd's in Parentheses)

atom	x	y	z	*U*(eq),[a] Å^2
Ni(1)	0.13895(8)	0.16008(7)	0.43255(4)	0.0132(2)
S(1)	0.1916(2)	0.3490(2)	0.04457(8)	0.0203(4)
S(2)	0.3344(2)	0.19283(15)	0.19005(8)	0.0169(4)
S(3)	0.0127(2)	0.36491(15)	0.18336(8)	0.0169(4)
S(4)	0.3277(2)	0.10661(14)	0.35598(8)	0.0155(4)
S(5)	−0.0266(2)	0.28713(15)	0.34714(8)	0.0156(4)
S(6)	0.3035(2)	0.04140(14)	0.51979(8)	0.0157(4)
S(7)	−0.0527(2)	0.20321(14)	0.50703(8)	0.0161(4)
S(8)	0.2624(2)	−0.03482(14)	0.68305(8)	0.0167(4)
S(9)	−0.0694(2)	0.11287(15)	0.67130(8)	0.0164(4)
S(10)	0.0757(2)	−0.0432(2)	0.81674(9)	0.0248(5)
C(1)	0.1800(6)	0.3038(5)	0.1352(3)	0.0155(17)
C(2)	0.2395(6)	0.1966(6)	0.2738(3)	0.0158(17)
C(3)	0.0856(6)	0.2764(6)	0.2705(3)	0.0146(17)
C(4)	0.1923(6)	0.0487(5)	0.5950(3)	0.0153(17)
C(5)	0.0324(6)	0.1183(6)	0.5892(3)	0.0148(17)
C(6)	0.0874(6)	0.0121(6)	0.7278(3)	0.0171(17)
Ni(2)	0.37752(8)	0.38228(7)	0.48051(4)	0.0135(2)
S(11)	0.4923(2)	0.5302(2)	0.09550(8)	0.0229(5)
S(12)	0.6123(2)	0.40030(15)	0.24706(8)	0.0167(4)
S(13)	0.2861(2)	0.56150(14)	0.22569(8)	0.0160(4)
S(14)	0.57755(15)	0.32873(14)	0.41143(8)	0.0152(4)
S(15)	0.2240(2)	0.50530(15)	0.38904(8)	0.0159(4)
S(16)	0.5343(2)	0.26335(15)	0.57114(8)	0.0163(4)
S(17)	0.1788(2)	0.42965(14)	0.55080(8)	0.0153(4)
S(18)	0.4805(2)	0.20463(15)	0.73468(8)	0.0166(4)
S(19)	0.1498(2)	0.35234(15)	0.71563(8)	0.0162(4)
S(20)	0.2834(2)	0.2314(2)	0.86721(9)	0.0252(5)
C(7)	0.4644(6)	0.4992(5)	0.1851(3)	0.0137(17)
C(8)	0.5007(6)	0.4110(6)	0.3262(3)	0.0141(17)
C(9)	0.3456(6)	0.4876(5)	0.3163(3)	0.0145(17)
C(10)	0.4155(6)	0.2772(5)	0.6447(3)	0.0140(17)
C(11)	0.2580(6)	0.3483(5)	0.6359(3)	0.0123(17)
C(12)	0.3018(6)	0.2610(6)	0.7775(3)	0.0172(17)
N(1)	0.2674(5)	0.8583(5)	0.0108(3)	0.0215(14)
N(2)	0.1719(6)	0.6936(5)	−0.0323(3)	0.0239(17)
N(3)	0.0603(6)	0.7989(5)	0.0673(3)	0.0282(17)
C(13)	0.1692(6)	0.7831(6)	0.0160(3)	0.0182(17)
C(14)	0.2762(8)	0.9434(8)	0.0695(5)	0.044(3)
C(15)	0.3869(7)	0.8434(6)	−0.0442(4)	0.0284(19)

[a] *U*(eq) = $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $[Me_2Gua][Ni(dmit)_2]_2$ (Esd's in Parentheses)

Ni(1)−S(4)	2.1676(18)	Ni(2)−S(17)	2.1546(19)
Ni(1)−S(5)	2.1535(17)	S(11)−C(7)	1.650(6)
Ni(1)−S(6)	2.1490(17)	S(12)−C(7)	1.722(6)
Ni(1)−S(7)	2.1534(18)	S(12)−C(8)	1.741(6)
S(1)−C(1)	1.662(6)	S(13)−C(7)	1.730(6)
S(2)−C(1)	1.722(6)	S(13)−C(9)	1.736(6)
S(2)−C(2)	1.737(6)	S(14)−C(8)	1.705(6)
S(3)−C(1)	1.720(6)	S(15)−C(9)	1.699(6)
S(3)−C(3)	1.741(6)	S(16)−C(10)	1.696(6)
S(4)−C(2)	1.708(6)	S(17)−C(11)	1.706(6)
S(5)−C(3)	1.707(6)	S(18)−C(10)	1.733(6)
S(6)−C(4)	1.681(6)	S(18)−C(12)	1.744(6)
S(7)−C(5)	1.686(6)	S(19)−C(11)	1.734(6)
S(8)−C(4)	1.736(6)	S(19)−C(12)	1.727(6)
S(8)−C(6)	1.726(6)	S(20)−C(12)	1.636(6)
S(9)−C(5)	1.745(6)	C(8)−C(9)	1.374(8)
S(9)−C(6)	1.722(6)	C(10)−C(11)	1.380(8)
S(10)−C(6)	1.651(6)	N(1)−C(13)	1.316(7)
C(2)−C(3)	1.370(8)	N(1)−C(14)	1.475(10)
C(4)−C(5)	1.394(8)	N(1)−C(15)	1.446(9)
Ni(2)−S(14)	2.1541(16)	N(2)−C(13)	1.337(8)
Ni(2)−S(15)	2.1630(17)	N(3)−C(13)	1.333(8)
Ni(2)−S(16)	2.1560(17)		

S(4)−Ni(1)−S(5)	93.43(7)	S(8)−C(6)−S(9)	114.4(3)
S(4)−Ni(1)−S(6)	87.55(7)	S(8)−C(6)−S(10)	121.2(3)
S(4)−Ni(1)−S(7)	176.71(7)	S(9)−C(6)−S(10)	124.4(4)
S(5)−Ni(1)−S(6)	177.54(6)	S(14)−Ni(2)−S(15)	93.20(7)
S(5)−Ni(1)−S(7)	86.30(7)	S(14)−Ni(2)−S(16)	86.04(6)
S(6)−Ni(1)−S(7)	92.85(7)	S(14)−Ni(2)−S(17)	178.39(7)
C(1)−S(2)−C(2)	97.5(3)	S(15)−Ni(2)−S(16)	178.49(7)
C(1)−S(3)−C(3)	97.5(3)	S(15)−Ni(2)−S(17)	87.81(7)
Ni(1)−S(4)−C(2)	102.0(2)	S(16)−Ni(2)−S(17)	92.98(7)
Ni(1)−S(5)−C(3)	101.9(2)	C(7)−S(12)−C(8)	97.0(3)
Ni(1)−S(6)−C(4)	102.9(2)	C(7)−S(13)−C(9)	97.5(3)
Ni(1)−S(7)−C(5)	102.7(2)	Ni(2)−S(14)−C(8)	102.2(2)
C(4)−S(8)−C(6)	97.5(3)	Ni(2)−S(15)−C(9)	102.3(2)
C(5)−S(9)−C(6)	97.0(3)	Ni(2)−S(16)−C(10)	102.7(2)
S(1)−C(1)−S(2)	123.3(3)	Ni(2)−S(17)−C(11)	102.6(2)
S(1)−C(1)−S(3)	123.1(3)	C(10)−S(18)−C(12)	97.6(3)
S(2)−C(1)−S(3)	113.5(3)	C(11)−S(19)−C(12)	97.6(3)
S(2)−C(2)−S(4)	123.4(3)	S(11)−C(7)−S(12)	122.5(3)
S(2)−C(2)−C(3)	115.7(4)	S(11)−C(7)−S(13)	123.8(3)
S(4)−C(2)−C(3)	120.8(4)	S(12)−C(7)−S(13)	113.7(3)
S(3)−C(3)−S(5)	122.5(3)	S(12)−C(8)−S(14)	122.2(3)
S(3)−C(3)−C(2)	115.7(4)	S(12)−C(8)−C(9)	116.4(4)
S(5)−C(3)−C(2)	121.8(4)	S(14)−C(8)−C(9)	121.4(4)
S(6)−C(4)−S(8)	123.8(3)	S(13)−C(9)−S(15)	123.7(3)
S(6)−C(4)−C(5)	120.9(4)	S(13)−C(9)−C(8)	115.3(4)
S(8)−C(4)−C(5)	115.3(4)	S(15)−C(9)−C(8)	121.0(4)
S(7)−C(5)−S(9)	123.4(3)	S(16)−C(10)−S(18)	123.3(3)
S(7)−C(5)−C(4)	120.7(4)	S(16)−C(10)−C(11)	121.1(4)
S(9)−C(5)−C(4)	115.9(4)	S(18)−C(10)−C(11)	115.6(4)
S(17)−C(11)−S(19)	123.1(3)	C(13)−N(1)−C(14)	120.0(5)
S(17)−C(11)−C(10)	120.7(4)	C(13)−N(1)−C(15)	122.2(5)
S(19)−C(11)−C(10)	116.3(4)	C(14)−N(1)−C(15)	117.0(5)
S(18)−C(12)−S(19)	113.0(3)	N(1)−C(13)−N(2)	120.6(5)
S(18)−C(12)−S(20)	122.7(3)	N(1)−C(13)−N(3)	120.9(5)
S(19)−C(12)−S(20)	124.3(4)	N(2)−C(13)−N(3)	118.4(5)

by automated Patterson methods and subsequent difference Fourier techniques[28] (DIRDIF-92). Refinement on F^2 was carried out by full-matrix least-squares techniques[29] (SHELXL-93); no observance criterion was applied during refinement. The hydrogen atoms were included in the refinement on calculated positions (N−H = 0.88 and C−H = 0.98 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter amounting to 1.2 and 1.5 times the value of the equivalent isotropic thermal parameter of their carrier atoms, for the amine and methyl hydrogen atoms, respectively. An empirical absorption/extinction correction was applied (DIFABS,[24] correction range 0.836–1.173). Weights were introduced in the final refinement cycles. Convergence was reached at $R1 = 0.0532$, for 363 parameters and the 4323 reflections above the $2.0\sigma(I)$ level, $wR2 = 0.1271$, for all 7102 unique reflections, $w = 1/[\sigma^2(F) + (0.0541P)^2]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$, and $S = 1.005$. A final difference Fourier map showed no residual density outside −0.75 and 0.82 e Å^{-3}. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 30.

Geometrical calculations and ORTEP illustrations were performed with PLATON.[27] All calculations were performed on a DECstation 5000 cluster. Positional parameters are listed in Table 4.

Results

Description of the Crystal Structures. $[Gua][Ni(dmit)_2]_2$. Table 2 lists the final fractional coordinates and the equivalent

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(28) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

(29) Sheldrick, G. M. SHELXL-93 Program for crystal structure refinement. University of Göttingen, Germany, 1993.

(30) Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

isotropic thermal parameters of the non-hydrogen atoms. Table 3 lists all relevant bond distances and bond angles. The three independent residues, two Ni(dmit)$_2$ units and one cation, with the labeling scheme used, are shown in Figure 1.

The observed Ni−S bond lengths vary from 2.145(6) to 2.167(6) Å, distances typical for Ni(dmit)$_2$ units having a formal charge of −0.5. The Ni(dmit)$_2$ units show a considerable deviation from planarity. The NiS$_4$ coordination geometry in Ni(1)(dmit)$_2$ is slightly distorted from square-planar to a tetrahedral configuration, the largest twist between the planes S(5)−Ni(1)−S(7) and S(4)−Ni(1)−S(6) being 2.9(3)°. The largest deviation from the least-squares planes through all 17 atoms of the units is found for S(7) of Ni(1)(dmit)$_2$ and C(9) of Ni(2)(dmit)$_2$, 0.065(5) and 0.05(1) Å, respectively.

The structure consists of two crystallographically independent Ni(dmit)$_2$ units in head-to-tail orientation with the Gua lying in between as is shown in Figure 1. The two independent Ni(dmit)$_2$ units make an angle of 145.51(12)°. The angle between the anions and the CN$_3$ plane of the cation is 82.7(9)° for Ni(1)(dmit)$_2$ and 81.2(9)° for Ni(2)(dmit)$_2$. Because of the head-to-tail orientation of the anions and the space group being $P\bar{1}$, the structure consists of two different types of stacks exhibiting different structural properties. Other compounds in which the M(dmit)$_2$ units crystallize in two nonequivalent stacks are [dmm][Ni(dmit)$_2$]$_2$[14c] (dmm = *N,N*-dimethylmorpholinium) and α-[N(CH$_3$)$_4$][Pd(dmit)$_2$]$_2$.[31] The two different types of stacks result in two different sheets of Ni(dmit)$_2$ units in the *ab* plane, shown in Figure 2a,b. Single black lines show the S···S contacts to be shorter than the sum of the van der Waals radii (3.70 Å). The units in the Ni(1)(dmit)$_2$ stack are slightly dimerized. This is a common feature in most [cation][Ni(dmit)$_2$]$_2$ salts. The sheet of Ni(1)(dmit)$_2$ stacks shows a two-dimensional network of short intra- and interstack S···S interactions. Two different intrastack contacts of 3.606(7) and 3.626(7) Å, respectively, were found, and several interstack contacts of which the shortest is 3.498(6) Å can be seen from Figure 2a. In the Ni(2)(dmit)$_2$ sheet several short interstack contacts were found of which the shortest is 3.488(7) Å. Although the distance between the planes through all 17 atoms of the units in the Ni(2)(dmit)$_2$ stack (3.59 Å) is not extremely large, no intrastack S···S interactions shorter than the sum of the van der Waals radii were found. The origin is probably the unfavorable modes of intermolecular overlap (see Figure 2b,c).

In addition to the short S···S contacts in the *ab* plane, there are also two contacts found in the *c* direction of the crystal structure (3.528(8) and 3.680(7) Å). In this direction the thione sulfur atoms are also connected to one or two hydrogen atoms of guanidinium by hydrogen bonds. To determine the hydrogen bonds the classification of Jeffrey et al.[32] was used. Tables (S8 and S9) and a figure (S1) of the S···S interactions and the hydrogen bonds are available as supplementary material.

[Me$_2$Gua][Ni(dmit)$_2$]$_2$. In Table 4 the final fractional coordinates and the equivalent isotropic thermal parameters of the non-hydrogen atoms are listed. Table 5 presents all relevant bond distances and bond angles. The three crystallographically independent residues, two Ni(dmit)$_2$ anions and one cation, with the labeling scheme used, are shown in Figure 3.

The Ni−S distance in the anions varies from 2.149(2) to 2.168(2) Å. This is the same range as was found for **1**. The distortion from planarity in these units is significantly larger than in the units of **1**. The highest out-of-plane deviation for the two units is found for the thione sulfur atoms S(10) and S(20), being 0.116(2) and 0.099(2) Å, respectively. A tetrahedral twist with a maximum of 4.10(9)° between the planes S(5)−Ni(1)−S(7) and S(4)−Ni(1)−S(6) describes the distortion of the NiS$_4$ coordination geometry from square-planar.

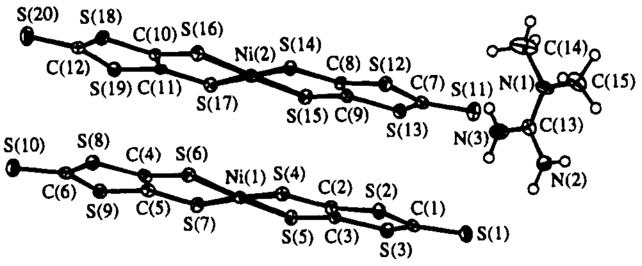

Figure 3. ORTEP 50% probability plot (PLATON[27]) of crystallographically independent units with atomic labeling scheme of [Me$_2$Gua][Ni(dmit)$_2$]$_2$.

Again two crystallographically independent Ni(dmit)$_2$ units are found, but in contrast to the units in **1**, these are lying in a face-to-face orientation (Figure 3). The angle between the least-squares planes through the two units is only 1.88(5)°, meaning that they are almost parallel. The angle between the anions and the C(13)N$_3$ plane of the cation is 77.3(3)° for Ni(1)(dmit)$_2$ and 75.4(3)° for Ni(2)(dmit)$_2$.

Because the crystallographically independent units are lying in a face-to-face orientation and the space group is $P\bar{1}$, the structure of **2** consists of only one type of stack. The Ni(dmit)$_2$ stacks form a sheet in the *ab* plane which contains intra- and interstack S···S contacts shorter than 3.70 Å, the sum of the van der Waals radii (Figure 4a). Four different intrastack contacts of 3.543(3), 3.676(2), 3.680(2), and 3.691(3) Å are found and several interstack contacts of which the shortest is 3.471(2) Å are depicted in Figure 4a. From the distances between the least-squares planes through all atoms of the units it can be seen that the anions are stacked in a slightly dimerized manner, as is frequently found in [cation][Ni(dmit)$_2$]$_2$ structures.

The modes of molecular overlap are shown in Figure 4b. Overlap B shows two Ni(dmit)$_2$ units that are turned a few degrees along the axis perpendicular on the plane of the units. This kind of turning is seen to a larger extent in α-[Et$_2$Me$_2$N][Ni(dmit)$_2$]$_2$[12] and [*N,N*-dimethylpiperidinium][Ni(dmit)$_2$]$_2$[14b] and is called the "spanning overlap" fashion. Both these salts remain two-dimensional conductors down to low temperature.

Similar to structure **1** intersheet contacts in the *c* direction are formed via S···S contacts (3.595(2) and 3.611(2) Å), as well as via N−H···S hydrogen bonds. Every hydrogen atom of the cation is bridged to one thione sulfur atom. Tables (S8 and S9) and a figure (S1) of the S···S interactions and the hydrogen bonds are available as supplementary material.

Intermolecular Orbital Overlap Integral Calculations. For a better understanding of the dimensionality of the compounds, intermolecular orbital overlaps were calculated. The intermolecular overlap integrals (*S*) between the LUMO's (lowest unoccupied molecular orbitals) of the neighboring Ni(dmit)$_2$ units were calculated using the scheme described by Kramer and Roothaan.[33] The molecular orbital of the neutral Ni(dmit)$_2$ was calculated using the extended Hückel program ICON8,[34]

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(31) Kobayashi, A.; Kim, H.; Sasaki, Y.; Murata, K.; Kato, R.; Kobayashi, H. *J. Chem. Soc, Faraday Trans.* **1990**, *86*, 361.

(32) Jeffrey, G. A.; Maluszynska, H.; Mitra, J. *Int. J. Biol. Macromol.* **1985**, *7*, 336

(33) (a) Kramer, G. J. Ph.D. Thesis, Leiden University, The Netherlands, 1988. (b) Roothaan, C. C. J. *J. Chem. Phys.* **1951**, *19*, 1445.

(34) Howell, J.; Rossi, A.; Wallace, D.; Haraki, K.; Hoffmann, R. ICON8 and FORTICON8, QCPE, Program for Extended Hückel Calculations.

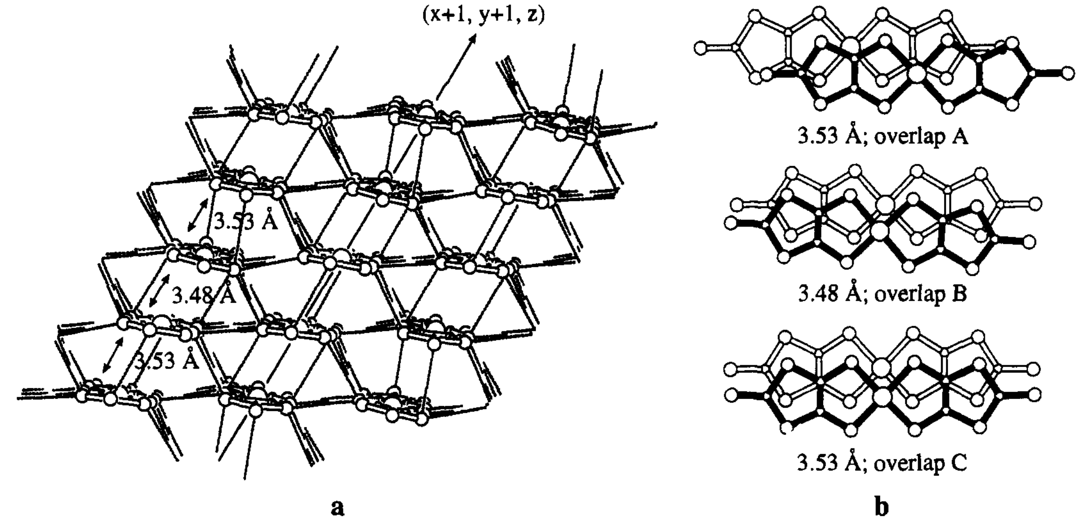

Figure 4. (a) Sheet of Ni(dmit)$_2$ units in the *ab* plane of [Me$_2$Gua][Ni(dmit)$_2$]$_2$. (b) Modes of intermolecular overlapping of Ni(dmit)$_2$ units in [Me$_2$Gua][Ni(dmit)$_2$]$_2$.

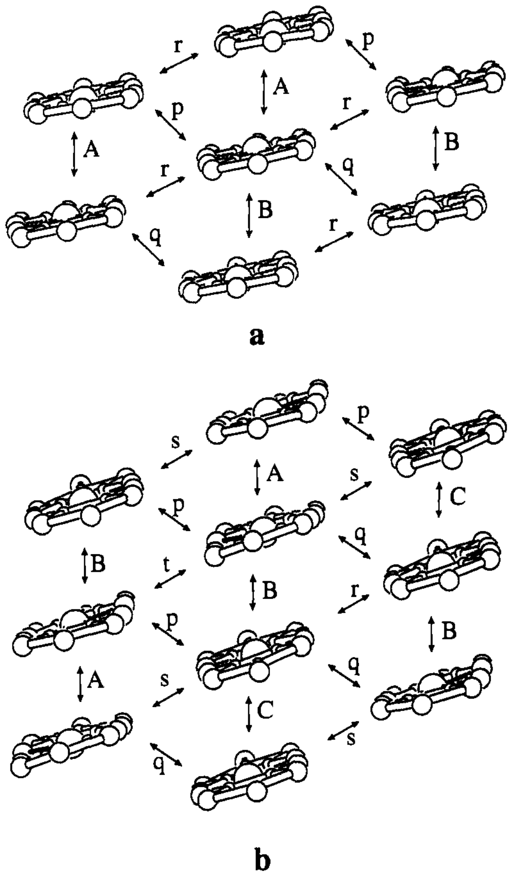

Figure 5. Scheme of the intermolecular orbital overlap integrals (*S*) of the LUMO's of the Ni(dmit)$_2$ units. (a) [Gua][Ni(dmit)$_2$]$_2$ (**1**) absolute overlap integral values ($\times 10^3$) are as follows. Sheet of Ni(1)(dmit)$_2$: *A*, 20.3; *B*, 2.5; *p*, 1.7; *q*, 3.4; *r*, 0.6. Sheet of Ni(2)(dmit)$_2$: *A*, 0.9; *B*, 17.8; *p*, 1.4; *q*, 3.0; *r*, 0.3. (b) [Me$_2$Gua][Ni(dmit)$_2$]$_2$ (**2**) absolute overlap integral values ($\times 10^3$): *A*, 1.4; *B*, 17.8; *C*, 17.7; *p*, 2.9; *q*, 2.8; *r*, 0.4; *s*, 0.3; *t*, 0.1.

with semi-empirical parameters taken from refs 35 and 36. The letters *A*, *B*, *C*, *p*, *q*, *r*, *s*, and *t* in Figure 5 represent the overlap integrals in the *ab* plane for **1** (Figure 5a) and **2** (Figure 5b).

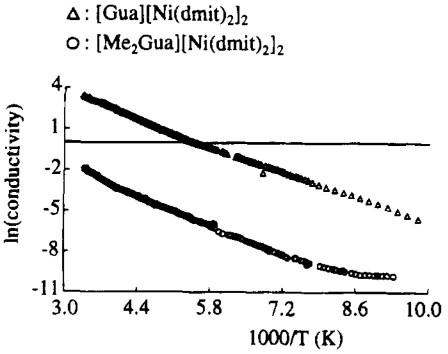

Figure 6. Temperature dependence of the conductivity of [Gua][Ni(dmit)$_2$]$_2$ and [Me$_2$Gua][Ni(dmit)$_2$]$_2$.

The absolute values of these integrals are given in the captions of Figure 5.

The orbital overlaps in the *c* direction are in the order of (1−5) × 10^{-4} for both compounds. This is thought to be not of significant influence on the conductivity.

Conductivity Measurements. Conductivity measurements were carried out at ambient pressure in the temperature range 300−100 K using the four point probe method. Four gold wires were glued on platelike crystals of 2.50 × 0.97 × 0.04 mm and 0.80 × 0.43 × 0.07 mm for **1** and **2**, respectively. Both compounds showed a semiconducting behavior in the whole temperature range (see Figure 6). Although the activation energy of both compounds is nearly the same, 0.12 eV for **1** and 0.13 eV for **2**, the room temperature conductivity differs significantly, i.e. 32 S·cm^{-1} for **1** and 0.15 S·cm^{-1} for **2**.

Discussion

The similarities between the Ni(1)(dmit)$_2$ sheet in structure **1** (Figure 2a) and the Ni(dmit)$_2$ sheet in **2** (Figure 4a) can be easily seen by comparison of the two structures. Both compounds contain two intrastack contacts between every two Ni(dmit)$_2$ units and several interstack contacts of approximately the same mean length. The contacts in these sheets lay upon the compounds a two-dimensional character.

It is known from the literature[37] that the orbital overlap in the stacking direction of Ni(dmit)$_2$ compounds depends on the interplanar distance and on the amount and the direction of the

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(35) McGlynn, S. P., Vanquickenborne, L. G., Konoshita, M., Carroll, D. G., Eds. *Introduction to Applied Quantum Chemistry*; Holt, Rhinehart and Winston Inc.: New York, 1972.

(36) Ballhausen, C. J., Gray, H. B., Eds. *Molecular Orbital Theory*; W. A. Benjamin, Inc.: New York, 1964.

shift of the Ni(dmit)$_2$ units toward each other. A shift along the long axis of the molecule results in a smaller overlap than a shift along the short axis. With this knowledge the differences in the orbital overlaps *A*, *B*, and *C* are easily understood. The fact that in compound **2** overlap *B* is not larger than overlap *C*, while the interplanar distance for *B* is 0.05 Å smaller, can be explained by the unfavorable tetrahedral twist of (especially) the sulfur atoms in the case of *B*. Regarding the interplanar distances, the molecule shifts and the orbital overlaps of the two stacks in compound **1**, the orbital overlaps in the stack of compound **2** were expected to be larger than the calculated values. These smaller overlaps can also be explained by unfavorable twisting of the atoms in the units in compound **2**.

The orbital overlap integrals in the interstack direction decrease when the units lie more side-by-side as is the case for *r*, *s*, and *t*. For *p* and *q* the units lie more or less above each other but are moved a few Å along the short axis of the molecule. Here the overlap can be rather large.[37]

The calculated intermolecular orbital overlap integrals indicate that there is no continuous large overlap ($>1 \times 10^{-2}$) in any direction. Therefore both compounds should be regarded as essentially "zero-dimensional". However, because of the intermediate overlaps in the *ab* plane ($>1 \times 10^{-3}$) the compounds can also be regarded as weak two-dimensional conductors. Unfortunately, the anisotropy of the conductivity in the compounds could not yet be confirmed by experiments due to the small dimensions of the crystals.

The deviations from planarity of the Ni(dmit)$_2$ units in both compounds not only result from the S···S interactions but also from the hydrogen bonds. Miyazaki et al. also found considerable deviations in Ni(dmit)$_2$ compounds containing H-bond-forming cations. The deviations appeared to be larger with stronger hydrogen bonds.[38,39]

The substitution of two of the hydrogen atoms of guanidinium by methyl groups results as expected in a different crystal structure. The origin for the much lower conductivity of compound **2** than in compound **1**, while the activation energies and the orbital overlap integrals in the compounds are of the same order, is as yet unclear, but it might be related to the differences in the hydrogen bonds. Further studies with Ni(dmit)$_2$ compounds in which four and six hydrogen atoms, respectively, of guanidinium are replaced by methyl groups are ongoing.

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Supplementary Material Available: Further details on the structure determinations, including tables of atomic coordinates for the hydrogen atoms, bond lengths and angles, S···S interactions and hydrogen bonds, and thermal parameters and a thermal motion ellipsoid plot for **1** and **2** (14 pages). Ordering information is given on any current masthead page.

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(37) Kobayashi, A.; Kim, H.; Sasaki, Y.; Kato, R.; Kobayashi, H. *Solid State Commun.* **1987**, *62*, 57.

(38) Miyazaki, A.; Izuoka, A.; Sugawara, T. *Mol. Cryst. Liq. Cryst.* **1992**, *216*, 217.

(39) Miyazaki, A.; Izuoka, A.; Sugawara, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2832.