Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-(2-Methoxy-2-oxoethyl)pyridinium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(III)

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.005 Å
R factor = 0.043
wR factor = 0.088
Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

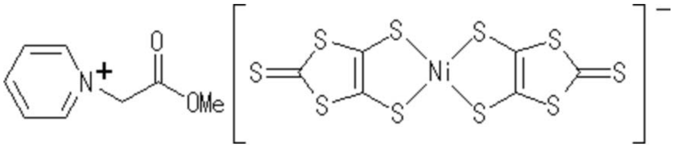
Received 15 December 2005
Accepted 3 January 2006
Online 11 January 2006

The title complex, $(C_8H_{10}NO_2)[Ni(C_3H_2S_5)_2]$, crystallizes with the cation sandwiched by two $[Ni(dmit)_2]^-$ anions (dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate). The crystal packing is stabilized by short intermolecular S$\cdots$S contacts between neighbouring anions and C—H$\cdots$O hydrogen bonds, which link the cations into ribbons extending along the *c* axis.

Comment

Transition metal complexes of 4,5-dimercapto-1,3-dithiole-2-thione (2-thioxo-1,3-dithiole-4,5-dithiolate, dmit) have received significant attention since the first open-shell molecular superconductor TTF$[Ni(dmit)_2]_2$ (TTF = tetrathiafulvalene; Bousseau *et al.*, 1986) and the first closed-shell molecular superconductor $[N(CH_3)_4][Ni(dmit)_2]_2$ (Kobayashi *et al.*, 1987) were reported. Although the closed-shell cations make no contribution to the conductivity, their sizes and shapes play a predominant role in influencing the crystal structure formation and, consequently, their electronic properties. To date, most of the closed-shell cations are tetraalkylammonium. Less attention has been paid to planar cations, although four planar aromatic cations have been reported (Miyazaki *et al.*, 1992; Veldhuizen *et al.*, 1997; Xu *et al.*, 2001). There are only a few reports of dmit complex salts with cations having electron-rich functional groups (Hirose *et al.*, 2002; Miyazaki *et al.*, 1993). We have reported previously (Tomono *et al.*, 2005) that the use of 3-methoxycarbonyl-1-methylpyridinium (3MMP) as cation resulted in the formation of cation pairs by C—H$\cdots$O hydrogen bonds in the crystal structure.

The synthesis of (3MMP)$[Ni(dmit)_2]$ has drawn our attention to the role of C—H$\cdots$O hydrogen bonding involving the carbonyl group, because this hydrogen bond may induce the construction of structures similar to (3MMP)$[Ni(dmit)_2]$. In order to explore new crystal structures of dmit complexes and to gain more insight into the structure-regulating ability of hydrogen bonding, the title complex, (I), where a carboxy group has been attached to the N atom of pyridine, has been synthesized and analysed by X-ray crystallography.



(I)

The asymmetric unit of (I) is shown in Fig. 1. The Ni—S distances range from 2.1569 (9) to 2.1721 (11) Å, with an

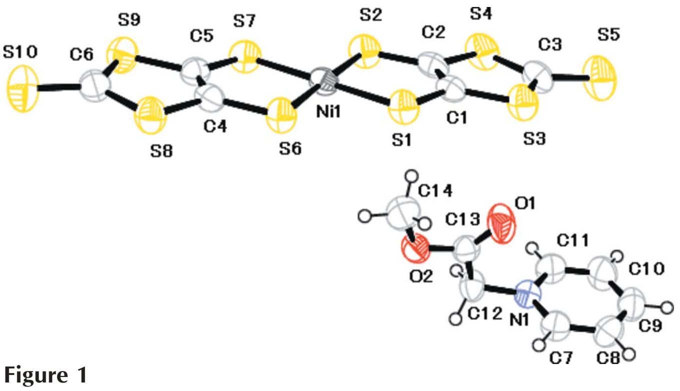


Figure 1
An *ORTEPIII* (Burnett & Johnson, 1996) view of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

average of 2.164 (4) Å, and the *cis*-S—Ni—S angles range from 86.13 (3) to 92.80 (4)° (Table 1). Therefore, the NiS_4 geometry is slightly distorted square-planar. The whole $[Ni(dmit)_2]^-$ anion is essentially planar, although the planes of the two coordinated $C_3S_5^{2-}$ ligands make a dihedral angle of 1.9 (5)°. In the crystal structure (Fig. 2), the anions and cations are almost parallel. The dihedral angle between the pyridine ring of the cation and plane of the anion is 8.44 (15)°. Two S···S contacts between the anions (Table 1), shorter than the sum of the van der Waals radii (3.70 Å), are shown in Fig. 2 by dotted lines. The packing of the cations (Fig. 3) exhibits weak intermolecular C—H···O hydrogen bonds (Table 2), which link the cations into ribbons extending along the *c* axis.

Additionally, the crystal packing is stabilized by the anion–cation Coulombic interaction, which can be estimated as a weak one. The electrical conductivity of the crystal measured by the two-probe alternating current method was 1.48×10^{-9} S cm^{-1} at room temperature, which is not very high among the (cation):$[Ni(dmit)_2]$ type of 1:1 complexes. The crystal structure, however, shows that the hydrogen-bond network is effective in forming one-dimensional arrays of cations, which consequently form one-dimensional arrays of $[Ni(dmit)_2]^-$ anions. As mentioned previously, the 1-(2-methoxy-2-oxoethyl)pyridinium cation is not planar but still possesses an ability to form a one-dimensional structure as a result of its hydrogen-bonded network, similar to the case of the 3MMP cation. Therefore, the planarity of the cation is not an important factor, while the presence of hydrogen bonds is the predominant factor for constructing separated domains of cations and anions.

Experimental

All reagents were of reagent grade and used without further purification. 1-(2-Methoxy-2-oxoethyl)pyridinium chloride was prepared as follows. To a mixture of pyridine (2.44 ml) and ethyl acetate (15 ml) was added methyl chloroacetate (2.74 ml), and the solution was stirred for 7 d at room temperature. The solvent was then removed by evaporation and the residue was washed with diethyl ether. $(Bu_4N)[Ni(dmit)_2]$ was synthesized according to the literature method (Steimecke *et al.*, 1979). By the interdiffusion of an acetone solution (25 ml) of $(Bu_4N)[Ni(dmit)_2]$ (0.05 mol) and a chloroform solution (50 ml) of 1-(2-methoxy-2-oxoethyl)pyridinium chloride (0.1 mol) at room temperature, dark-green plate crystals of suitable size for X-ray diffraction and conductivity measurement were obtained after 7 d.

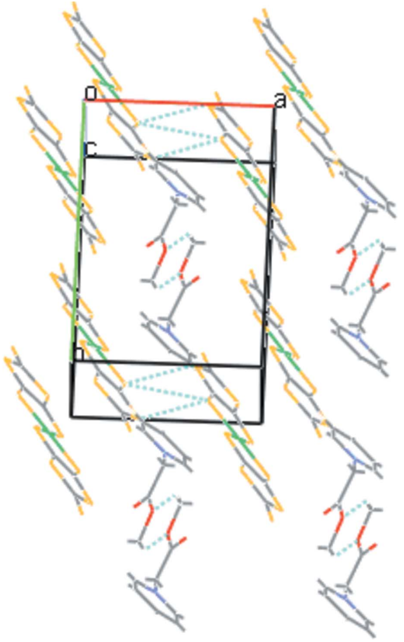


Figure 2
The crystal packing of (I). Dashed lines indicate short S···S contacts and C—H···O hydrogen bonds.

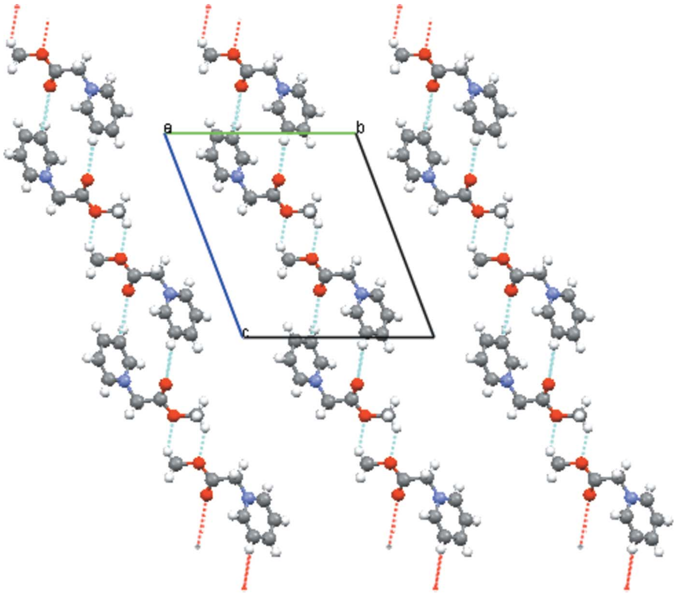


Figure 3
Hydrogen-bonded (dashed lines) network of the cations in (I).

Crystal data

$(C_8H_{10}NO_2)[Ni(C_3H_2S_5)_2]$
$M_r = 603.54$
Triclinic, $P\bar{1}$
$a = 8.1870$ (9) Å
$b = 11.2783$ (12) Å
$c = 13.0752$ (14) Å
$\alpha = 69.190$ (2)°
$\beta = 80.777$ (2)°
$\gamma = 89.274$ (2)°
$V = 1112.7$ (2) Å^3
$Z = 2$
$D_x = 1.801$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2126 reflections
$\theta = 2.8$–27.3°
$\mu = 1.82$ mm^{-1}
$T = 273$ (2) K
Plate, dark green
$0.20 \times 0.09 \times 0.04$ mm

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Data collection

Bruker SMART APEX CCD-detector diffractometer
ω scans
Absorption correction: Gaussian (*XPREP* in *SAINT*; Bruker, 2001)
$T_{\min} = 0.756$, $T_{\max} = 0.934$
6648 measured reflections
4674 independent reflections
3072 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\max} = 27.4°$
$h = -10 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.088$
$S = 0.89$
4674 reflections
254 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—S1	1.723 (3)	C5—S9	1.747 (3)
C1—S3	1.732 (3)	C6—S10	1.631 (4)
C2—S2	1.724 (4)	C6—S8	1.721 (4)
C2—S4	1.745 (3)	C6—S9	1.744 (4)
C3—S4	1.720 (4)	Ni1—S6	2.1569 (9)
C3—S3	1.727 (3)	Ni1—S1	2.1615 (10)
C4—S6	1.707 (3)	Ni1—S2	2.1671 (9)
C4—S8	1.746 (3)	Ni1—S7	2.1721 (11)
C5—S7	1.720 (3)		
S6···S8$^{\rm i}$	3.5466 (15)	S6···S6$^{\rm i}$	3.6508 (18)
S6—Ni1—S1	86.13 (3)	S6—Ni1—S7	92.66 (4)
S6—Ni1—S2	178.61 (4)	S1—Ni1—S7	178.73 (4)
S1—Ni1—S2	92.80 (4)	S2—Ni1—S7	88.42 (4)

Symmetry code: (i) $-x+1, -y+2, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···O1$^{\rm ii}$	0.93	2.50	3.132 (4)	125
C14—H14B···O2$^{\rm iii}$	0.96	2.49	3.285 (5)	140

Symmetry codes: (ii) $-x+1, -y+1, -z$; (iii) $-x+1, -y+1, -z+1$.

All H atoms were positioned geometrically and allowed to ride on their attached atoms, with C—H distances in the range 0.93–0.97 Å and $U_{\rm iso} = 1.2U_{\rm eq}$(C) [or $1.5U_{\rm eq}$(C) for methyl groups].

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*, *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* (Sakai, 2002), *ORTEPIII* and *MERCURY*.

References

Bousseau, M., Valade, L., Legros, J.-P., Cassoux, P., Garbauskas, M. & Interrante, L. V. (1986). *J. Am. Chem. Soc.* **108**, 1908–1916.

Bruker (2001). *SAINT* (Version 6.22) and *SMART* (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Hirose, T., Imai, H., Naito, T. & Inabe, T. (2002). *J. Solid. State Chem.* **168**, 535–546.

Kobayashi, A., Kim, H., Sasaki, Y., Kato, R., Kobayashi, H., Moriyama, S., Nishio, Y., Kajita, K. & Sasaki, W. (1987). *Chem. Lett.* pp. 1819–1822.

Miyazaki, A., Izuka, A. & Sugawara, T. (1992). *Bull. Chem. Soc. Jpn*, **65**, 2528–2530.

Miyazaki, A., Izuoka, A. & Sugawara., T. (1993). *Bull. Chem. Soc. Jpn*, **66**, 2832–2839.

Molecular Structure Corporation (2001). *TEXSAN*. Version 1.11r1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sakai, K. (2002). *KENX*. Tokyo University of Science, Japan.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Steimecke, G., Sieler, H. J., Kirmse, R. & Hoyer, E. (1979). *Phosphorous Sulfur*, **7**, 49–55.

Tomono, K., Sasaki, Y. & Miyamura, K. (2005). *Acta Cryst.* E**61**, m18–m20.

Veldhuizen, Y. S. J., Jerome, D., Paulus, P. M., Haasnoot, J. G. & Reedijk, J. (1997). *Inorg. Chem.* **36**, 4930–4937.

Xu, W., Zhang, D.-Q., Yang, C.-H., Jin, X.-L., Li, Y.-F. & Zhu, D.-B. (2001). *Synth. Met.* **122**, 409–412.

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