

Tetra-*n*-butylammonium bis(1,2-dimercaptoethene-1,2-dicarbonitrilato-*S,S'*)nickel(III)

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The crystal structure of the title compound, (C₁₆H₃₆N)⁺[Ni(C₄N₂S₂)₂]⁻, shows stacking of the dimerized anions, surrounded by columns of cations.

Comment

1,3-Dithiolate complexes of transition metals are planar electronic acceptors and have received attention in connection with their magnetic and electrical conducting properties. The discovery of ferromagnetic ordering in (NH₄)[Ni(mnt)₂]·H₂O

below 4.5 K (Coomber *et al.*, 1996) has especially stimulated interest in *M*(mnt)₂-based compounds (mnt = S₂C₄N₂²⁻ = dimercaptomaleodinitrilate). These structures of several tetraalkylammonium salts of the Ni(mnt)₂ anions have been reported so far, most of which are Ni^{II} salts represented as (R₄N)₂[Ni(mnt)₂], where *R* is Me (Eisenberg & Ibers, 1965), Et (Mahadevan *et al.*, 1984) and ⁿBu (Kobayashi & Sasaki, 1977), while (Et₄N)[Ni(mnt)₂] is the only example of an Ni^{III} salt (Kobayashi & Sasaki, 1977).

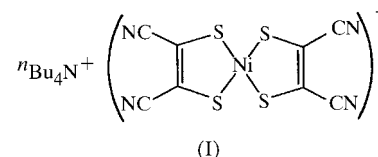


Fig. 1 presents an *ORTEP* (Spek, 2000) diagram and Fig. 2 a packing diagram of (nBu₄N)[Ni(mnt)₂], (I). The intramolecular Ni–S and S–C distances (Table 1) in the anion are consistent with the corresponding values in [Ni(mnt)₂]²⁻ (Mahadevan *et al.*, 1984). The anions form dimers and are stacked in a columnar fashion along the *c* axis. Important intermolecular distances between the anions are listed in Table 2. Within the dimer, the long molecular axes of the anions are parallel, being in a slipped configuration such that the central metal atoms are positioned above the S atom of the other anion with an Ni···S distance of 3.7148 (9) Å. This stacking mode is often observed in [Ni(mnt)₂]²⁻ salts. The Ni···Ni distance within the dimer is 3.9963 (8) Å. The long axis of an adjacent molecule makes an angle of *ca* 65° with that in the dimer, interacting *via* an Ni···S contact of 3.715 (1) Å.

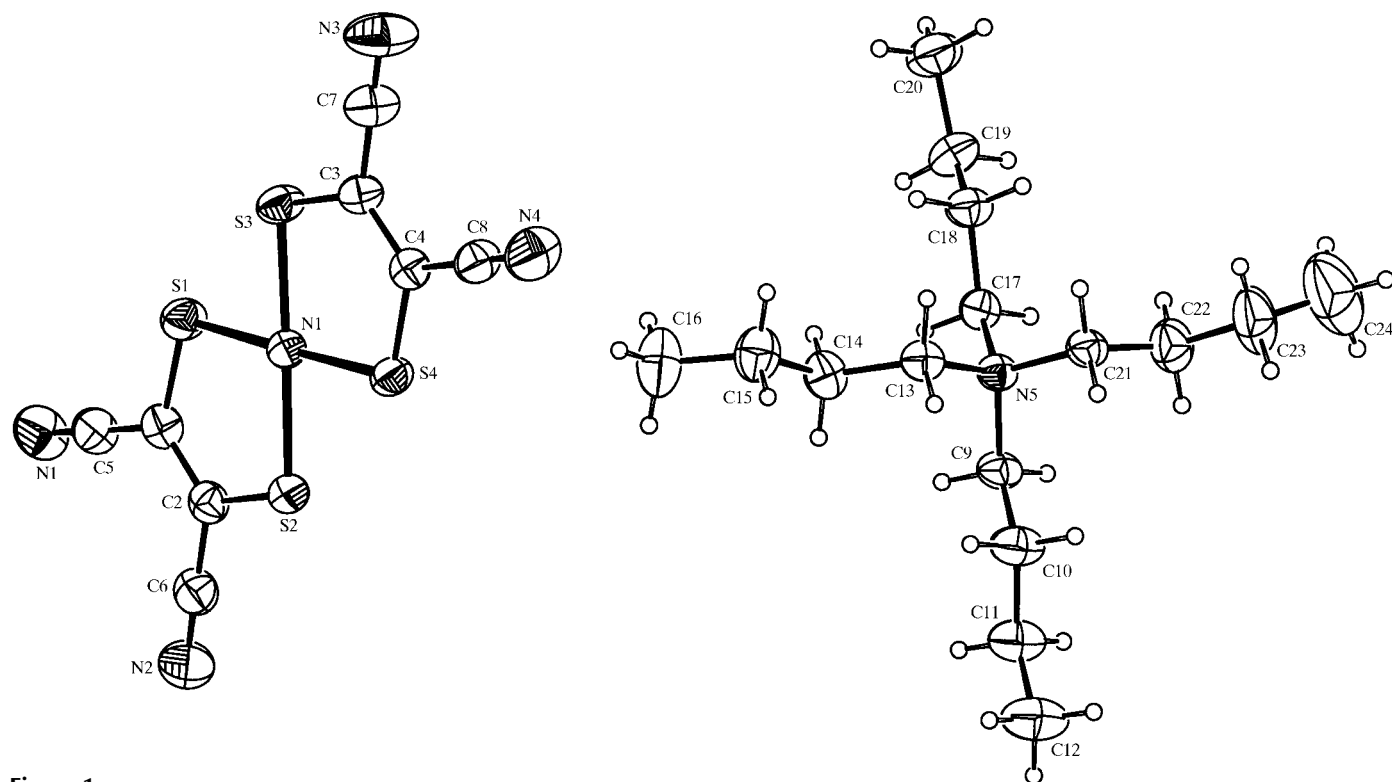


Figure 1

ORTEP (Spek, 2000) drawing of (I). The displacement ellipsoids are drawn at the 30% probability level.

The intradimer Ni···Ni distance is 4.5263 (8) Å. Measurements of electrical conductivity revealed that the material is an insulator, which is consistent with the acceptor arrangement as shown above. The anion stack is surrounded by columns of cations. The *n*Bu groups in the cation have an all-*trans* conformation.

We note finally that a report was found on a corresponding Au^{III} complex, (*n*Bu₄N)[Au(mnt)₂] (Saluschke *et al.*, 1996) in the Cambridge Structural Database (refcode MLNLAU02). Although no coordinates are given, it is highly probable that the complex is isomorphous with the present compound, judging from the similarity in the space group and cell parameters (*C*2/*c*, *a* = 30.853, *b* = 13.923, *c* = 15.759 Å, β = 115.78°).

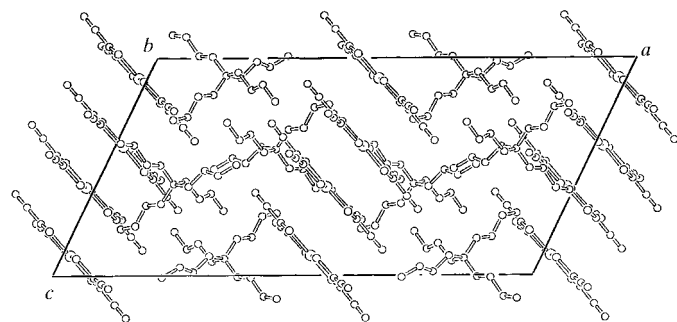


Figure 2
Packing diagram of (I). H atoms have been omitted for clarity.

Experimental

The title compound was purchased from Tokyo Kasei Kogyo Co. Ltd. Single crystals were grown by vapour diffusion of ether into acetonitrile solutions of the compound.

Crystal data

(C₁₆H₃₆N)[Ni(C₄N₂S₂)₂]
M_r = 581.52
 Monoclinic, *C*2/*c*
a = 30.879 (6) Å
b = 13.793 (5) Å
c = 15.669 (5) Å
 β = 115.68 (2)°
V = 6014 (3) Å³
Z = 8
D_x = 1.284 Mg m⁻³
D_m = 1.286 Mg m⁻³

D_m measured by flotation in toluene/MeI
 Mo Kα radiation
 Cell parameters from 24 reflections
 θ = 14.9–15.0°
 μ = 0.944 mm⁻¹
T = 296.2 K
 Prismatic, black
 0.38 × 0.30 × 0.18 mm

Table 1
Selected geometric parameters (Å, °).

Ni—S1	2.1465 (9)	S3—C3	1.712 (3)
Ni—S2	2.1458 (9)	S4—C4	1.714 (3)
Ni—S3	2.1409 (9)	N1—C5	1.142 (5)
Ni—S4	2.1437 (9)	N2—C6	1.137 (4)
S1—C1	1.718 (3)	N3—C7	1.131 (5)
S2—C2	1.719 (3)	N4—C8	1.139 (5)
S1—Ni—S2	92.27 (4)	S3—Ni—S4	92.24 (4)
S1—Ni—S3	87.13 (4)	Ni—S1—C1	103.7 (1)
S1—Ni—S4	178.52 (4)	Ni—S2—C2	103.6 (1)
S2—Ni—S3	178.44 (4)	Ni—S3—C3	103.7 (1)
S2—Ni—S4	88.40 (4)	Ni—S4—C4	103.4 (1)

Data collection

Rigaku AFC-7R diffractometer
 ω-2θ scans
 Absorption correction: analytical (Molecular Structure Corporation, 1999a)
T_{min} = 0.704, *T_{max}* = 0.809
 7332 measured reflections
 6914 independent reflections
 4451 reflections with *F*² > 2σ(*F*²)

R_{int} = 0.015
 θ_{max} = 27.5°
h = 0 → 40
k = 0 → 17
l = -20 → 18
 3 standard reflections
 every 150 reflections
 intensity decay: 0.79%

Refinement

Refinement on *F*²
R(*F*) = 0.041
wR(*F*²) = 0.105
S = 1.275
 4451 reflections
 307 parameters

H-atom parameters not refined
w = 1/[σ²(*F_o*²) + (0.05*P*)²]
 where *P* = [max(*F_o*², 0) + 2*F_c*²]/3
 (Δ/σ)_{max} = 0.020
 Δρ_{max} = 0.39 e Å⁻³
 Δρ_{min} = -0.35 e Å⁻³

Table 2
Intermolecular distances (Å).

Ni···S2 ⁱ	3.7148 (9)	Ni···Ni ⁱ	4.5263 (8)
Ni···S4 ⁱⁱ	3.715 (1)	Ni···Ni ⁱⁱ	3.9963 (8)

Symmetry codes: (i) -*x*, *y*, ½ - *z*; (ii) -*x*, 1 - *y*, 1 - *z*.

H atoms were fixed at ideal positions with *B_{iso}* values of 6.0 Å².

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999b); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1387). Services for accessing these data are described at the back of the journal.

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