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N-Methylquinolinium Bis(6,7-dihydro-5*H*-1,4-dithiepine-2,3-dithiolato)nickelate(III)

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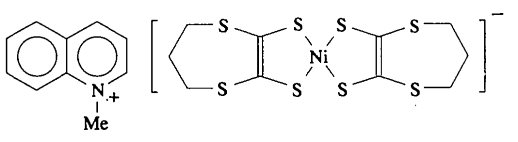
Abstract

In the title compound, $(C_{10}H_{10}N)[Ni(C_5H_6S_4)_2]$, there are two independent anions. In both, the central Ni atom lies on a $\bar{1}$ centre and displays square-planar coordination. The shortest S···S contact between anions is 3.535 (2) Å.

Comment

Since metal complexes of 4,5-dimercapto-1,3-dithiole-2-thionate (DMIT) were first reported to exhibit high conductivities, a massive research effort has centred on the design and synthesis of similar complexes (Cassoux *et al.*, 1991). The multi-sulfur 1,2-dithiolene complexes $[Ni(DDDT)_2]^{n-}$ (DDDT = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) (Vance, Bereman, Bordner, Hatfield & Helms, 1985; Welch, Bereman & Singh, 1989) and $[Ni(PDDDT)_2]$ (PDDT = 6,7-dihydro-5*H*-1,4-dithiepine-2,3-dithiolate) (Bereman & Lu, 1993; Yao, You & Yang, 1994) have been synthesized and studied. It is believed that molecular interactions through sulfur–sulfur contacts form effective electrical conduction pathways in these crystal phases. In addition, the introduction of various organic countercations is of interest because of the possibilities of modifying the interactions between the anions (Cornelissen, Creyghton, de Graaf, Haasnoot & Reedijk, 1991). To investigate the effects of the cation on the crystal packing motif and properties, we prepared the title complex, (I), for comparison with the corresponding 2-(dimethylaminostyryl)pyridylmethyl salt, (II) (Zuo, Yao, Xu, You & Huang, 1995).



(I)

Crystals of (I) contain two independent anions, each with the Ni atom lying on a centre of symmetry surrounded by a square plane of four S atoms (Fig. 1). The average Ni—S, S—C_{sp^2} and C═C bond lengths in the $Ni(S_2C_2)_2$ core of (I) [2.140 (2), 1.729 (5) and 1.354 (7) Å, respectively] agree well with the corresponding values [2.148 (1), 1.726 and 1.337 Å, respectively] in (II).

The four anions that comprise the contents of a single unit cell are each oriented in a different direction. In the *ab* face of the unit cell, Ni(1) atoms lie at the origin and Ni(2) atoms at the centre of each face; the same is true for the *ac* face. In both planes the adjacent anions are tilted in different directions. The closest S···S contact between different anions is 3.535 (2) Å,

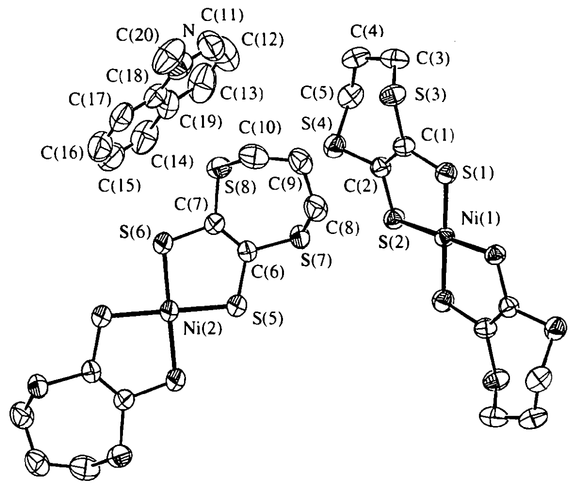


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

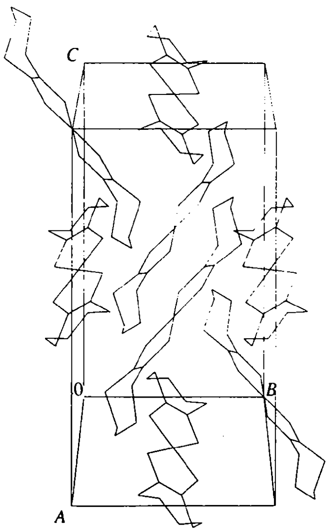


Fig. 2. The unit-cell diagram of (I) looking down the *a* axis.

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occurring between S(2) and S(7). It is shorter than the van der Waal's diameter of sulfur (3.70 Å). The shortest Ni···Ni distance is 9.013 (3) Å.

Experimental

An acetonitrile solution (30 cm^3) of [Bu_4N][Ni(PDDT)$_2$] (Yao, You & Yang, 1994) (0.061 mmol) was mixed with an acetonitrile solution (15 cm^3) of *N*-methylquinolinium iodide (0.061 mmol). Brown plate-shaped crystals were obtained by slow evaporation at room temperature.

Crystal data

($C_{10}H_{10}N$)[Ni($C_5H_6S_4$)$_2$]
$M_r = 591.58$
Monoclinic
$P2_1/c$
$a = 15.275$ (2) Å
$b = 9.588$ (4) Å
$c = 17.717$ (2) Å
$\beta = 106.78$ (1)°
$V = 2484$ (1) Å^3
$Z = 4$
$D_x = 1.58$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8.57–14.86°$
$\mu = 1.441$ mm^{-1}
$T = 296$ K
Plate
0.60 × 0.40 × 0.30 mm
Brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*TEXSAN*; Molecular Structure Corporation, 1985)
$T_{min} = 0.858$, $T_{max} = 1.000$
4841 measured reflections
4682 independent reflections

3495 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.0102$
$\theta_{max} = 25°$
$h = 0 \rightarrow 18$
$k = -11 \rightarrow 0$
$l = -21 \rightarrow 21$
3 standard reflections monitored every 300 reflections
intensity decay: 1.1%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.068$
$S = 1.78$
3495 reflections
274 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 1.28$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni(1)	0	1/2	1/2	3.20 (4)
S(1)	−0.0736 (1)	0.6368 (1)	0.55519 (8)	3.92 (5)
S(2)	0.1216 (1)	0.5250 (1)	0.59706 (8)	3.47 (5)
S(3)	−0.0318 (1)	0.8355 (1)	0.68622 (8)	4.44 (6)
S(4)	0.1863 (1)	0.7121 (1)	0.73400 (8)	4.23 (6)
C(1)	0.0072 (4)	0.6990 (5)	0.6383 (3)	3.4 (2)
C(2)	0.0941 (3)	0.6504 (5)	0.6562 (3)	3.3 (2)
C(3)	−0.0114 (5)	0.7766 (6)	0.7862 (3)	5.0 (3)
C(4)	0.0854 (5)	0.7915 (6)	0.8384 (3)	4.9 (3)
C(5)	0.1522 (4)	0.6868 (6)	0.8227 (3)	4.7 (2)
Ni(2)	1/2	1	1/2	3.31 (4)
S(5)	0.3837 (1)	0.8668 (1)	0.47980 (8)	3.82 (5)
S(6)	0.4517 (1)	1.1270 (1)	0.5786 (1)	4.49 (6)
S(7)	0.2340 (1)	0.8197 (1)	0.54873 (8)	4.18 (6)
S(8)	0.3101 (1)	1.1019 (2)	0.6612 (1)	5.20 (7)
C(6)	0.3245 (3)	0.9262 (5)	0.5425 (3)	3.3 (2)
C(7)	0.3549 (4)	1.0405 (5)	0.5869 (3)	3.8 (2)
C(8)	0.1359 (4)	0.9319 (7)	0.5256 (3)	5.2 (3)
C(9)	0.1262 (4)	1.0299 (7)	0.5913 (4)	5.0 (3)
C(10)	0.1948 (5)	1.1476 (7)	0.6096 (4)	6.1 (3)
N	0.3403 (4)	1.2471 (6)	0.8484 (3)	5.9 (3)
C(11)	0.2917 (6)	1.169 (1)	0.8820 (5)	7.8 (4)
C(12)	0.3199 (7)	1.038 (1)	0.9141 (6)	8.8 (5)
C(13)	0.4022 (7)	0.9939 (8)	0.9101 (5)	8.5 (4)
C(14)	0.5442 (5)	1.0246 (7)	0.8701 (5)	6.6 (3)
C(15)	0.5935 (5)	1.1082 (9)	0.8366 (5)	7.2 (4)
C(16)	0.5601 (6)	1.237 (1)	0.8070 (4)	7.0 (4)
C(17)	0.4786 (5)	1.2846 (7)	0.8102 (4)	5.8 (3)
C(18)	0.4262 (4)	1.2048 (6)	0.8443 (3)	4.3 (2)
C(19)	0.4568 (5)	1.0725 (7)	0.8760 (4)	5.4 (3)
C(20)	0.3042 (6)	1.3795 (7)	0.8141 (5)	8.3 (4)

Table 2. *Selected geometric parameters (Å, °)*

Ni(1)—S(1)	2.141 (1)	S(2)—C(2)	1.725 (5)
Ni(1)—S(2)	2.150 (1)	S(3)—C(3)	1.799 (6)
S(1)—C(1)	1.731 (5)	S(4)—C(5)	1.810 (6)
S(3)—C(1)	1.757 (5)	C(3)—C(4)	1.508 (9)
S(4)—C(2)	1.764 (5)	Ni(2)—S(5)	2.132 (1)
C(1)—C(2)	1.357 (7)	Ni(2)—S(6)	2.137 (1)
C(4)—C(5)	1.514 (8)	S(5)—C(6)	1.720 (5)
S(6)—C(7)	1.738 (5)	S(7)—C(6)	1.747 (5)
S(7)—C(8)	1.794 (6)	S(8)—C(7)	1.751 (5)
S(8)—C(10)	1.789 (7)	C(6)—C(7)	1.350 (7)
C(8)—C(9)	1.536 (8)	C(9)—C(10)	1.509 (9)
C(1)—S(1)—Ni(1)	105.1 (2)	S(1)—Ni(1)—S(2)	90.75 (5)
C(1)—S(3)—C(3)	104.8 (2)	C(2)—S(2)—Ni(1)	104.9 (2)
C(2)—C(1)—S(1)	119.3 (4)	C(2)—S(4)—C(5)	105.6 (3)
S(1)—C(1)—S(3)	114.2 (3)	C(2)—C(1)—S(3)	126.2 (4)
C(1)—C(2)—S(4)	125.0 (4)	C(1)—C(2)—S(2)	119.5 (4)
C(4)—C(3)—S(3)	115.8 (4)	S(2)—C(2)—S(4)	115.4 (3)
C(4)—C(5)—S(4)	116.7 (4)	C(3)—C(4)—C(5)	114.7 (5)
S(5)—Ni(2)—S(6)	91.33 (5)	C(6)—S(5)—Ni(2)	105.1 (2)
C(7)—S(6)—Ni(2)	104.2 (2)	C(6)—S(7)—C(8)	105.0 (3)
C(7)—S(8)—C(10)	103.9 (3)	C(7)—C(6)—S(5)	119.3 (4)
C(7)—C(6)—S(7)	125.6 (4)	S(5)—C(6)—S(7)	114.8 (3)
C(6)—C(7)—S(6)	119.7 (4)	C(6)—C(7)—S(8)	124.6 (4)
C(9)—C(8)—S(7)	116.8 (4)	C(9)—C(10)—S(8)	116.5 (5)
C(10)—C(9)—C(8)	114.1 (5)	S(6)—C(7)—S(8)	115.4 (3)

Data collection was performed using *CONTROL* software (Molecular Structure Corporation, 1986). The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983). The Ni atom was located in an *E* map and the remaining non-H atoms were located using *DIRDIF* (Beurskens, 1984). H atoms were placed in geometrically calculated positions with C—H = 0.95 Å, but were not included in the refinement. The structure was refined by full-matrix least-squares techniques with anisotropic displacement parameters for all non-H atoms. All calculations were performed on a VAX3100 computer using the *TEXSAN* (Molecular Structure Corporation, 1985) program package.

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Lists of structure factors, anisotropic displacement parameters, least-squares-planes data, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1192). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyanobis(1,10-phenanthroline)copper(II) Tricyanomethanide Dihydrate

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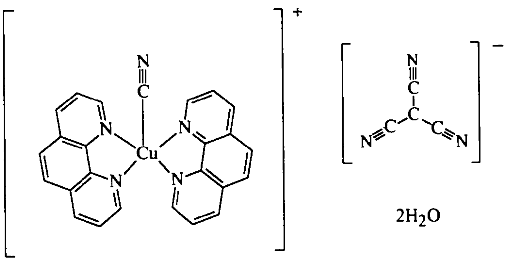
Abstract

The crystal structure of the title complex, $[Cu(CN)(C_{12}H_8N_2)_2][C(CN)_3].2H_2O$, is formed by discrete $[Cu(phen)_2(CN)]^+$ cations, tcm anions and uncoordinated water molecules [phen = 1,10-phenanthroline, tcm = tricyanomethanide, $C(CN)_3^-$]. The Cu atom is coordinated by four N atoms (from two phen molecules) and by one C atom (from the cyanide group in the equatorial plane) in the form of a distorted trigonal bipyramid.

Comment

The title compound, (I), was prepared and its crystal structure solved as part of our study concerning changes in the shape of the $[Cu(phen)_2X]^+$ cation (X^- = pseudohalide anion) caused by variation of the out-of-sphere anion.



(I)

Recently, we determined the structure of $[Cu(phen)_2(NCS)][C(CN)_3]$ with X^- = NCS^- (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996). The tcm anion did not enter the inner coordination sphere of the Cu atom, probably because of steric repulsion. Rather than the bulky NCS^- anion, we investigated the smaller CN^- group to find out whether the large tcm anion would coordinate to the Cu atom to form a six-coordinate species. The result is the title complex, (I), with a five-coordinate Cu atom.

Fig. 1 shows one formula unit with the atomic labelling scheme. The Cu atom is coordinated by four N atoms from two phen molecules and by one C atom from the CN^- group. The coordination polyhedron is in the form of a distorted trigonal bipyramid with the C atom in the equatorial plane. Neither the tcm anion nor the two water molecules enter the inner coordination sphere. The same $[Cu(phen)_2(CN)]^+$ cation has been found in the structures of $[Cu(phen)_2(CN)]NO_3.H_2O$ (Anderson, 1975) and $[Cu^{II}(phen)_2(CN)][Cu^I(phen)_2(CN)_2].5H_2O$ (Dunaj-Jurčo *et al.*, 1993).

The two out-of-plane Cu—N bonds in (I) (Cu—N21 and Cu—N31) are practically of the same length (average 2.002 Å) and are almost collinear [N21—Cu—N31 = 169.92 (12)°]. The two in-plane Cu—N bonds (Cu—N11 and Cu—N41) are not significantly different in length either (average 2.106 Å) but they are longer than the out-of-plane Cu—N distances, on average by 0.104 Å. The third in-plane bond [Cu—

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