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A Novel Nickel-Containing Chain-Like Polymer: $[\{Ni(NH_3)_4\}Ni\{S_2C{=}C(CN)_2\}_2]_\infty$

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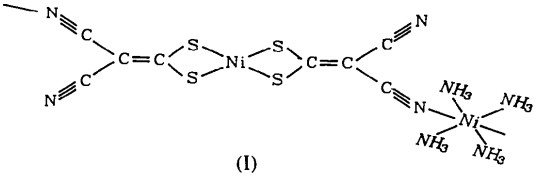
Abstract

The title complex, *catena*-poly[{tetraamminenickel(II)}-μ-(1,1-dicyanoethene-2,2-dithiolato-*N*:*S*,*S*′)-nickel(II)-μ-(1,1-dicyanoethene-2,2-dithiolato-*S*,*S*′:*N*)], is a chain-like polymer of $S_2C{=}C(CN)_2^{2-}$ (i-mnt^{2-}) units. One cyano group of i-mnt^{2-} in the anionic moiety $Ni\{S_2C{=}C(CN)_2\}_2^{2-}$ is bonded to the Ni atom of the cationic moiety $Ni(NH_3)_4^{2+}$ to form an infinite –(i-mnt)–Ni–(i-mnt)–Ni(NH$_3$)$_4$– zigzag chain. The packing of the chains gives rise to a corrugated layer structure perpendicular to the *a* axis. The other cyano group of i-mnt^{2-} is hydrogen bonded to two NH$_3$ ligands to link adjacent chains within the same layer as well as between adjacent layers.

Comment

Metal-containing chain-like polymers have unusual electronic, magnetic and optical properties (Sheats, Carraher & Pittman, 1985; Hanack *et al.*, 1986; Hanack, Deger & Lange, 1988; Pollagi, Stoner, Dallinger, Gilbert & Hopkins, 1991; Hanack, Gül & Subramanian, 1992; Anderson, Martin & Bradley, 1994). The planar conjugated polydentate ligands 1,1-dicyanoethene-2,2- dithiolate (i-mnt^{2-}) and 1,2-dicyanoethene-1,2-dithiolate (mnt^{2-}) may connect metal moieties to form this kind of polymer, but so far only their metal monoanions have been synthesized and structurally characterized (Werden, Billig & Gray, 1966; Fackler & Coucouvanis, 1966; Coucouvanis, Baenziger & Johnson, 1974; Endres, Keller, Moroni & Nöthe, 1979; Hummel, 1987; Clemenson, Underhill, Hursthouse & Short, 1988; Clemenson, Underhill, Kobayashi & Kobayashi, 1990). In our attempt to obtain metal-containing chain-like complexes, the title polymer, (I), was synthesized from the reaction of $K_2[S_2C{=}C(CN)_2]$, $NiCl_2.6H_2O$ and $(NH_4)_2CO_3$ in aqueous solution.


(I)

The striking structural feature of the polymer is the Ni—N bond, Ni from $Ni(NH_3)_4^{2+}$ and N from one of the cyano groups of i-mnt^{2-}, linking the $Ni(NH_3)_4^{2+}$ cation and the $Ni\{S_2C{=}C(CN)_2\}_2^{2-}$ anion to form an infinite –(i-mnt)–Ni–(i-mnt)–Ni(NH$_3$)$_4$– zigzag chain. There are two Ni atoms in the asymmetric unit of the polymer, Ni1 of NiN$_6$ and Ni2 of NiS$_4$. Ni1 is located at the centre of symmetry (0, 1/2, 1/2) and surrounded by a slightly distorted octahedron of six N atoms, four from ammonia molecules and two from the cyano groups of two i-mnt^{2-} moieties. The Ni—N(i-mnt^{2-}) bond length is 2.088 (4) Å, insignificantly shorter than those of Ni—N(NH$_3$) [2.102 (4) and 2.110 (4) Å]. Ni2 is located at the symmetry centre (0, 0, 0) and coordinated in a square-planar arrangement by four S atoms of two i-mnt^{2-} units with regular Ni—S bond lengths [2.204 (1) and 2.206 (1) Å]. There are two polymer chains in a cell, related to each other through a 2$_1$ axis along the *a* axis and extending infinitely onto the *bc* planes. The packing of the polymer chains gives rise to a corrugated layer structure along the *a* axis with the shortest Ni···Ni distance to the adjacent layers being 4.759 (1) Å. The hydrogen bonds from the N atom of i-mnt^{2-} (not bonded to Ni) to the ammonia molecules occur in two different directions to link adjacent chains within the same layer [N3^{iii}···N1 3.148 (7), N3^{iii}···H1 2.281 Å and N3^{iii}···H1—N1 151.18°; symmetry code: (iii) $-x$, $2 - y$, $1 - z$], and between adjacent layers [N3^{iv}···N2 3.343, N3^{iv}···H4 2.398 Å and N3^{iv}···H4—N2 172.26°; symmetry code: (iv) $1/2 - x$, $y - 1/2$, $3/2 - z$].

The length of the triple bond of the C≡N bonded to the Ni atom [1.130 (6) Å] is comparable to the length of the other C≡N bond [1.135 (6) Å] (invoved in hydrogen bonds) and the lengths of the C≡N bonds in [Ag(PPh$_3$)$_2$][Ni(i-mnt)$_2$] [1.09 (2), 1.13 (3), 1.11 (2) and 1.10 (3) Å] (Coucouvanis, Baenziger & Johnson, 1974). The C=C double bond length of 1.386 (6) Å is longer than that of [Ag(PPh$_3$)$_2$]$_2$[Ni(i-mnt)$_2$] [1.28 (2) Å], in which the CN groups are not bonded.

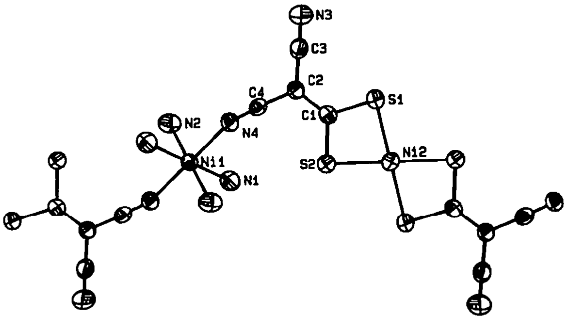


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

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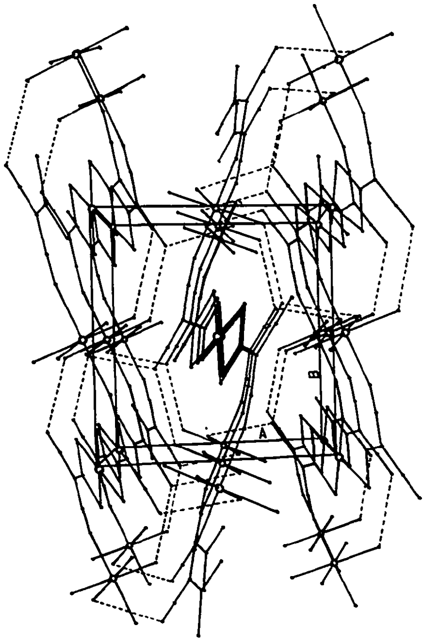

Fig. 2. Packing diagram showing the corrugated layer structure along the *a* axis. The hydrogen bonds link adjacent chains within a layer and adjacent layers.

Experimental

A mixture of $K_2[S_2C{=}C(CN)_2]$, $NiCl_2.6H_2O$ and $(NH_4)_2CO_3$ (molar ratio 1:1:2) in water was stirred for 2 min at room temperature, then filtered. The filtrate was kept in air for 10 d, after which crystals suitable for X-ray analysis were obtained.

Crystal data

$[Ni_2(C_4N_2S_2)_2(NH_3)_4]$
$M_r = 465.88$
Monoclinic
$P2_1/n$
$a = 9.539\,(2)$ Å
$b = 9.684\,(1)$ Å
$c = 10.218\,(1)$ Å
$\beta = 106.26\,(1)°$
$V = 906.1\,(5)$ Å^3
$Z = 2$
$D_x = 1.71$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.31–14.71°$
$\mu = 2.538$ mm^{-1}
$T = 296$ K
Block
$0.15 \times 0.15 \times 0.10$ mm
Dark brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan
$T_{min} = 0.873$, $T_{max} = 1.000$
2216 measured reflections
2118 independent reflections
1353 observed reflections $[I > 3\sigma(I)]$

$R_{int} = 0.00817$
$\theta_{max} = 27°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 300 reflections
intensity decay: 0.3%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.053$
$S = 1.28$
1353 reflections
104 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1989)
Extinction coefficient: 1.923×10^{-7} (secondary)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	B_{eq}
Ni1	0	1/2	1/2	2.65 (3)
Ni2	0	1	0	3.06 (4)
S1	0.1071 (2)	1.1096 (1)	0.1908 (1)	3.42 (5)
S2	0.0095 (2)	0.8359 (1)	0.1518 (1)	3.97 (5)
N1	−0.1960 (5)	0.5737 (4)	0.3656 (4)	3.8 (2)
N2	−0.0714 (5)	0.5583 (5)	0.6689 (4)	4.3 (2)
N3	0.2694 (7)	1.1191 (5)	0.5774 (5)	5.9 (3)
N4	0.0918 (5)	0.6948 (4)	0.4944 (4)	3.5 (2)
C1	0.0932 (5)	0.9561 (4)	0.2704 (5)	2.8 (2)
C2	0.1417 (5)	0.9333 (5)	0.4097 (5)	2.9 (2)
C3	0.2129 (7)	1.0367 (5)	0.5021 (5)	3.6 (2)
C4	0.1173 (5)	0.8010 (5)	0.4614 (4)	3.0 (2)

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

Ni1—N4	2.088 (4)	N3—C3	1.135 (6)
Ni1—N1	2.110 (4)	N4—C4	1.130 (6)
Ni1—N2	2.102 (4)	C1—C2	1.386 (6)
Ni2—S1	2.204 (1)	C2—C3	1.412 (7)
Ni2—S2	2.206 (1)	C2—C4	1.430 (6)
S1—C1	1.717 (5)	N3^{i}···N1	3.148 (7)
S2—C1	1.709 (5)	N3^{ii}···N2	3.343 (7)
N4—Ni1—N4^{iii}	180.00	C1—S2—Ni2	85.8 (2)
N4—Ni1—N2	90.9 (2)	C4—N4—Ni1	163.3 (4)
N4—Ni1—N2^{iii}	89.1 (2)	C2—C1—S2	125.1 (4)
N4—Ni1—N1	88.8 (2)	C2—C1—S1	125.2 (4)
N4—Ni1—N1^{iii}	91.2 (2)	S2—C1—S1	109.7 (3)
N2—Ni1—N1	90.7 (2)	C1—C2—C3	122.2 (4)
N2^{iii}—Ni1—N1	89.3 (2)	C1—C2—C4	118.7 (4)
N2—Ni1—N1^{iii}	89.3 (2)	C3—C2—C4	119.1 (4)
S1—Ni2—S2	78.88 (5)	N3—C3—C2	179.2 (6)
S1^{iv}—Ni2—S2	101.12 (5)	N4—C4—C2	175.6 (5)
C1—S1—Ni2	85.6 (2)		

Symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $-x, 1-y, 1-z$; (iv) $-x, 2-y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN HKL* (Molecular Structure Corporation, 1989). Structure solution: *MITHRIL* (Gilmore, 1984). Structure refinement: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1237). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,2′-Iminodipyridinium Tetrachlorocuprate(II)

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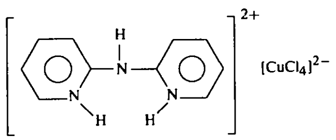
Abstract

The title structure, $(C_{10}H_{11}N_3)[CuCl_4]$, consists of isolated diprotonated 2,2′-iminodipyridinium cations and $CuCl_4^{2-}$ anions. The anions assume a flattened tetrahedral geometry, with *trans* Cl—Cu—Cl bond angles of 137.3 (1) and 139.2 (1)°. The Cu—Cl bond distances average 2.249 Å. The non-planar cations assume an *S-trans* configuration with one ring twisted 16.3 (6)° out of the central C—N—C plane and the other ring twisted 32.0 (7)° in the opposite sense. The cation configuration represents a balance of intramolecular repulsions and external hydrogen-bonding interactions, with N(1) and N(3) hydrogen bonding to Cl(3) [3.080 (5) Å] and Cl(2) [3.167 (5) Å], respectively, on one anion, while N(9) is involved in a weaker hydrogen bond to Cl(1) [3.486 (3) Å] of a second anion.

Comment

The title compound, (I), was prepared as part of our study of the structural characteristics of organoammonium salts of Cu^{II} halides.



(I)

An illustration of the asymmetric unit is shown in Fig. 1. Each pyridinium ring is nearly planar (maximum deviation 0.017 Å), but is twisted 45.7° with respect to the other. This twist is caused by repulsion of the H atoms on C(7) and N(9). The *S-trans* conformation minimizes internal electrostatic repulsions and provides maximum hydrogen-bonding capability. This twist comes at the expense of hyperconjugation of the amine C—N bonds. The hydrogen-bonding scheme (Fig. 2) indicates relative inefficiency as shown by the non-linearity of the N—H···Cl interaction.

The structural chemistry of more than 60 salts containing $CuCl_4^{2-}$ anions has been summarized recently (Halvorson, Patterson & Willett, 1990). The degree of flattening was shown to be roughly related to the strength of the *A*—H···Cl hydrogen bonding. The distortion in the present compound is in the middle of the observed range, consistent with the presence of a limited number of hydrogen-bonding interactions.

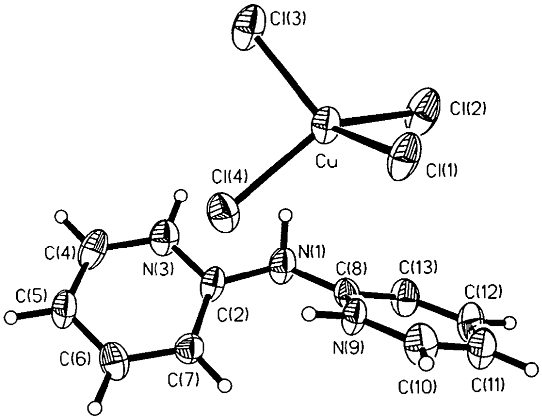


Fig. 1. Displacement ellipsoid plot illustrating the asymmetric unit of the title structure. Ellipsoids are plotted at the 50% probability level.