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## Key indicators

Single-crystal X-ray study

T = 298 K

Mean  $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$ 

R factor = 0.097

wR factor = 0.176

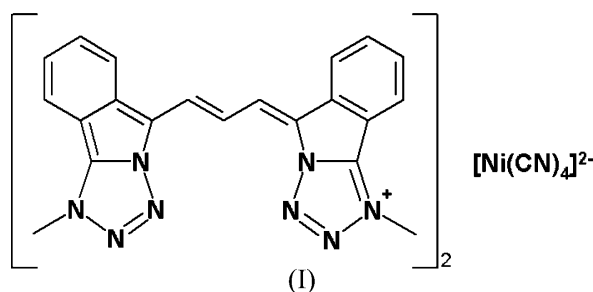
Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Bis{1-methyl-5-[3-(1-methyl-1*H*-tetrazolo[5,1-*a*]-isoindol-5-yl)allylidene]-5*H*-tetrazolo[5,1-*a*]isoindol-1-ium} tetracyanonickelate(II)**

The molecular structure of the title compound,  $(\text{C}_{21}\text{H}_{17}\text{N}_8)_2[\text{Ni}(\text{CN})_4]$ , consists of two organic cations,  $\text{C}_{21}\text{H}_{17}\text{N}_8^+$  or  $[\text{MTIT}]^+$ , and a centrosymmetric inorganic dianion,  $[\text{Ni}(\text{CN})_4]^{2-}$ . In the crystal structure, the ions stack along the *b* axis and are connected by a number of  $\text{C}-\text{H}\cdots\text{N}$  hydrogen bonds.

## Comment

The study of the title compound, (I), was undertaken to establish its three-dimensional structure. To our knowledge only one other cyanine molecular complex,  $\text{cy}^+[\text{AuCl}_2]^-$ , has been reported to date (Falkenberg *et al.*, 1973).



The molecular structure of (I), consisting of two 1-methyl-5-[3-(1-methyl-1*H*-tetrazolo[5,1-*a*]isoindol-5-yl)-allylidene]-5*H*-tetrazolo[5,1-*a*]isoindol-1-ium monocations,  $[\text{MTIT}]^+$ , and an  $[\text{Ni}(\text{CN})_4]^{2-}$  dianion, is illustrated in Fig. 1. Selected bond lengths and angles are given in Table 1. The organic  $[\text{MTIT}]^+$  cation is planar and the C–C bonds lengths range from 1.370 (9) to 1.457 (7) Å, indicating the aromaticity of the dye molecule. Both  $[\text{MTIT}]^+$  cations possess identical geometry in the carbon–nitrogen skeleton.

The geometry of the  $[\text{Ni}(\text{CN})_4]^{2-}$  anion is typical for a square-planar Ni atom with four CN groups (Table 1). The Ni atom lies on a centre of symmetry. These planar anions are located parallel to one another at a distance of 6.83 (3) Å, forming stacks. The stacks are inclined to the *ac* plane at 60 and 120°, and are staggered (Fig. 2).

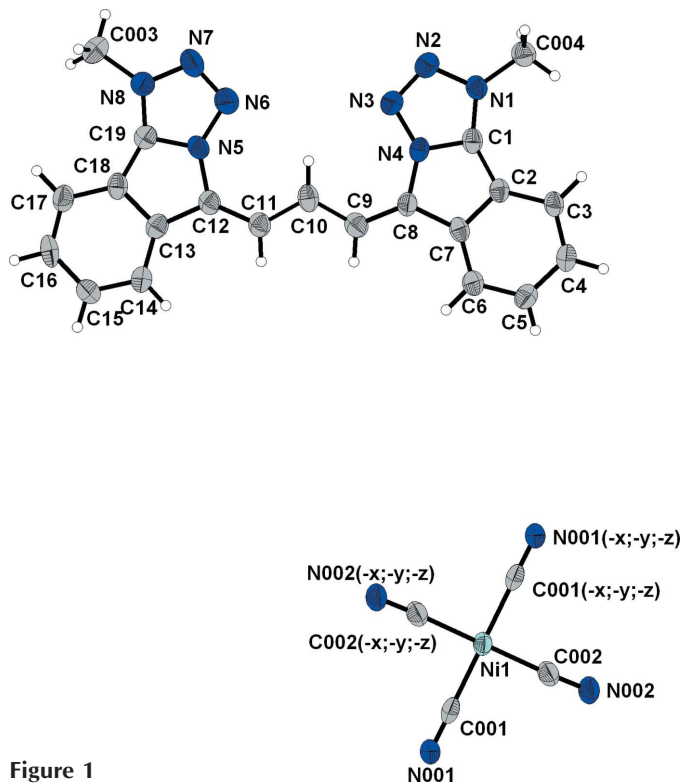
The  $[\text{MTIT}]^+$  dye cations are stacked stepwise with two opposite orientations. The  $[\text{Ni}(\text{CN})_4]^{2-}$  anion is located between these steps, and the Ni $\cdots$ C distances are 3.80 (4) and 3.739 (15) Å, thus indicating additional interactions of the Ni atoms with the conjugated system of the dye (Fig. 3).

The N atoms of the CN groups are bound to the  $[\text{MTIT}]^+$  dye cations *via* C–H $\cdots$ N hydrogen bonds (Table 2). Each  $[\text{Ni}(\text{CN})_4]^{2-}$  anion has three N $\cdots$ H contacts with two dye cations that lie in one plane. These cations are positioned axial to the Ni atoms. One more pair of N $\cdots$ H contacts is formed with two dye cations that are almost perpendicular to the

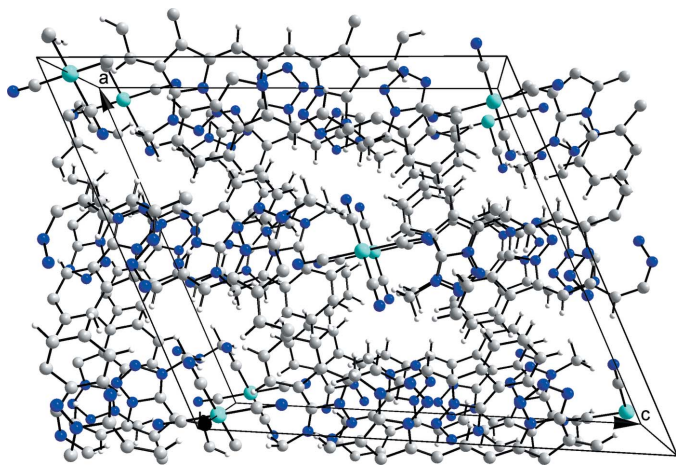
Received 28 October 2005

Accepted 28 November 2005

Online 14 December 2005



**Figure 1**  
A view of the molecular structure of (I), showing the labelling scheme and displacement ellipsoids at the 50% probability level.



**Figure 2**  
A view along *b* of the crystal packing of compound (I).

plane of the  $[\text{Ni}(\text{CN})_4]^{2-}$  complex anion. This situation is shown in Fig. 4 and details are given in Table 2.

In view of these stabilizing interactions, (I) can be considered not as a simple cation–anion salt but as a molecular complex with specific intermolecular interactions.

## Experimental

The starting material, MTIT perchlorate, was prepared according to a known protocol (Babichev & Romanov, 1975). The title compound, (I), was prepared from equimolar quantities of  $[\text{MTIT}]^+\cdot\text{ClO}_4^-$  and  $\text{K}_2[\text{Ni}(\text{CN})_4]$  in an acetonitrile/propanol/water system (Yegorova *et al.*, 2002).  $[\text{MTIT}]^+\cdot\text{ClO}_4^-$  (306 mg, 0.64 mmol) in acetonitrile (150 ml) was mixed with  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (120 mg) in a 2-propanol–

water mixture (1:1, 30 ml). This mixture was heated to boiling point for 10 min and then cooled slowly to 273 K. Formation of a black–green crystalline precipitate was observed. This crystalline product was decanted, washed with water and 2-propanol, and dried at 313 K. The amount of Ni in (I) was determined by ICP atomic emission spectroscopy, and no K was found in the analysed samples. By IR spectroscopy, the cyanine fingerprint was observed with the addition of a CN band at  $2110\text{ cm}^{-1}$ . The characteristic perchlorate bands at 630 and  $1100\text{ cm}^{-1}$  were absent. The UV–vis spectra showed the dye bands at 590 (shoulder) and 636 nm, and a new band, at 770 nm, was attributed to an  $\text{Ni}^{\text{II}}$  transition.

## Crystal data

$(\text{C}_{21}\text{H}_{17}\text{N}_8)_2[\text{Ni}(\text{CN})_4]$   
 $M_r = 925.61$   
 Monoclinic,  $P2_1/n$   
 $a = 16.296(2)\text{ \AA}$   
 $b = 7.5708(7)\text{ \AA}$   
 $c = 18.537(3)\text{ \AA}$   
 $\beta = 115.42(2)^\circ$   
 $V = 2065.6(6)\text{ \AA}^3$   
 $Z = 2$

$D_x = 1.488\text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 4688 reflections  
 $\theta = 0\text{--}29.2^\circ$   
 $\mu = 0.53\text{ mm}^{-1}$   
 $T = 298\text{ K}$   
 Prism, black–green  
 $0.2 \times 0.2 \times 0.1\text{ mm}$

## Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1995)  
 $T_{\text{min}} = 0.901$ ,  $T_{\text{max}} = 0.949$   
 18746 measured reflections  
 4672 independent reflections

3172 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.069$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -21 \rightarrow 21$   
 $k = -9 \rightarrow 9$   
 $l = -24 \rightarrow 21$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.097$   
 $wR(F^2) = 0.176$   
 $S = 1.33$   
 4672 reflections  
 314 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 6.0123P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.45\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.73\text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ni1–C001	1.868 (7)	N5–C19	1.352 (6)
Ni1–C002	1.888 (5)	N5–N6	1.371 (7)
N1–N2	1.371 (5)	N5–C12	1.415 (7)
N1–C004	1.462 (7)	N6–N7	1.290 (7)
N1–C1	1.344 (7)	N7–N8	1.353 (7)
N2–N3	1.297 (7)	N8–C003	1.463 (6)
N3–N4	1.364 (5)	N8–C19	1.344 (7)
N4–C1	1.352 (7)	N001–C001	1.160 (9)
N4–C8	1.407 (7)	N002–C002	1.148 (7)
C001–Ni1–C002	90.9 (2)	N6–N7–N8	109.5 (5)
C001–Ni1–C001 <sup>i</sup>	180	N7–N8–C19	109.7 (4)
C001–Ni1–C002 <sup>i</sup>	89.1 (2)	N7–N8–C003	121.8 (5)
C002–Ni1–C002 <sup>i</sup>	180	C003–N8–C19	128.5 (5)
C1–N1–C004	130.0 (4)	N1–C1–C2	146.5 (5)
N2–N1–C1	109.4 (4)	N1–C1–N4	104.2 (4)
N2–N1–C004	120.5 (4)	N4–C1–C2	109.3 (5)
N1–N2–N3	108.9 (4)	N4–C8–C9	124.8 (5)
N2–N3–N4	106.5 (3)	N4–C8–C7	103.5 (4)
N3–N4–C8	137.0 (4)	N5–C12–C11	125.5 (5)
N3–N4–C1	111.0 (4)	N5–C12–C13	102.9 (4)
C1–N4–C8	112.0 (4)	N5–C19–C18	108.9 (5)
N6–N5–C12	136.9 (4)	N5–C19–N8	104.0 (4)
N6–N5–C19	110.5 (4)	N8–C19–C18	147.1 (5)
C12–N5–C19	112.5 (5)	Ni1–C001–N001	179.5 (5)
N5–N6–N7	106.2 (4)	Ni1–C002–N002	177.6 (5)

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

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C003—H00E...N001 <sup>ii</sup>	0.96	2.59	3.532 (9)	166
C3—H3...N002 <sup>iii</sup>	0.98	2.54	3.509 (7)	171
C4—H4...N001 <sup>iv</sup>	0.97	2.52	3.421 (7)	154
C004—H00A...N002 <sup>iii</sup>	0.96	2.49	3.394 (7)	157
C10—H10...N3	0.93	2.56	3.184 (8)	125
C10—H10...N6	0.93	2.56	3.193 (7)	126
C14—H14...N001 <sup>v</sup>	0.90	2.61	3.489 (7)	165

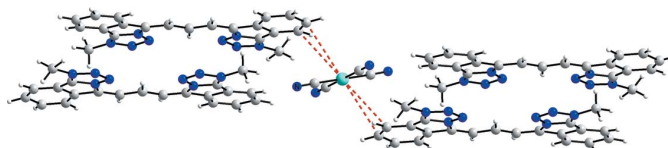
Symmetry codes: (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $-x + 1, -y, -z$ ; (iv)  $x + 1, y, z$ ; (v)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ .

The methyl H atoms in the [MTIT]<sup>+</sup> cation were included in calculated positions and refined as riding atoms [C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ ]. The remainder of the H atoms were located in difference Fourier syntheses; the atomic parameters were initially refined and then held fixed (C—H = 0.88–0.98 Å), with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

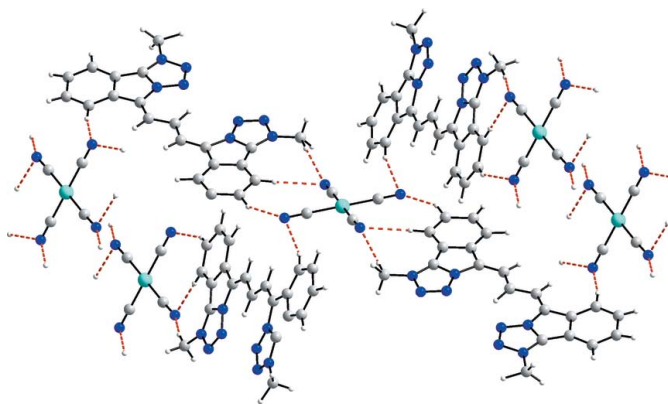
Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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**Figure 3**  
A view of the interaction of the Ni atom with the  $\pi$ -system of the dye cation (dashed lines).



**Figure 4**  
A view of the C—H...N interactions (dashed lines) in the crystal structure of compound (I).

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