A Hofmann pyridine complex: poly[tetra-μ-cyano-dipyridinemanganese(II)nickel(II)]

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The title compound, [MnNi(CN)$_4$(C$_5$H$_5$N)$_2$], has a layered structure of a two-dimensional network complex Mn(py)$_2$Ni(CN)$_4$, in which linkages of cyanide between the equatorial coordination sites of octahedral Mn^{II} ions (site symmetry $2/m$) and those of square planar Ni^{II} ions (site symmetry $2/m$) form a square mesh network. Pyridine ligands (located on mirror planes) coordinate to the axial sites of the Mn^{II} ions from both sides of the network.
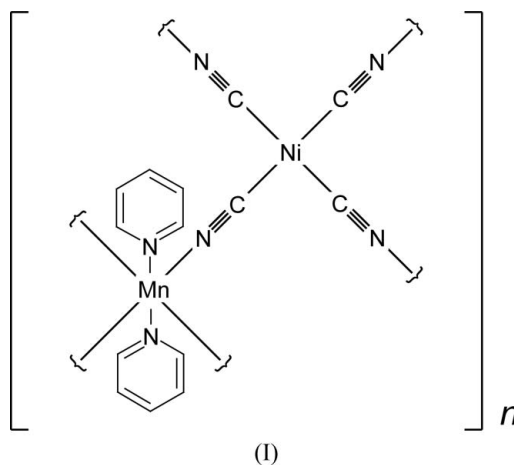
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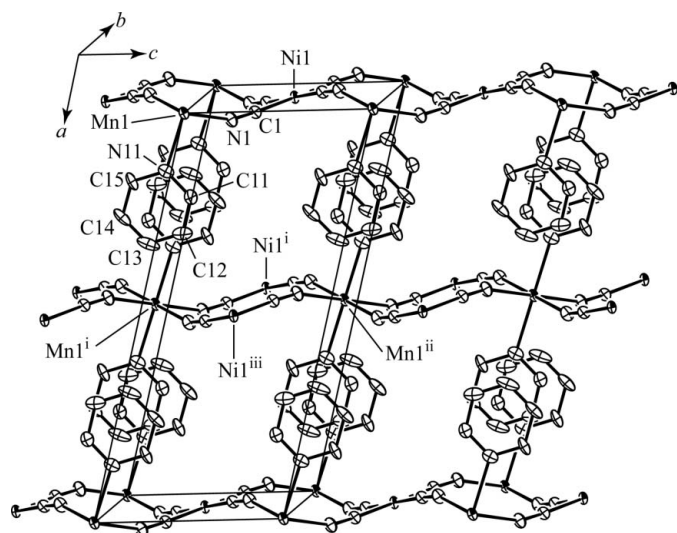The title compound, Mn(py)$_2$Ni(CN)$_4$, (I), is one of the Hofmann pyridine complexes M(py)$_2$Ni(CN)$_4$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd) (Akyüz et al., 1973; Morehouse et al., 1977). The name, Hofmann pyridine complex, comes from its structural similarity to the metal complex host of the Hofmann-type clathrate M(NH$_3$)$_2$Ni(CN)$_4$·2G (G = a guest; benzene, aniline, etc; Hofmann et al., 1897; Powell et al., 1949; Iwamoto, 1984). In 1996, co-operative spin-crossover behaviour was discovered in Fe(py)$_2$Ni(CN)$_4$, which is a member of the Hofmann pyridine complexes (Kitazawa et al., 1996). Moreover, its deuterated compound showed an unusual transition temperature shift (Hosoya et al., 2003). These findings triggered intensive research on its related compounds (Kitazawa et al., 2003; Molnár et al., 2004; Niel et al., 2001; Tayagaki et al., 2005; Bonhommeau et al., 2005). In this study, we have investigated the magnetic properties of (I), which has the largest number of unpaired electrons of the Hofmann pyridine complexes. The present structure determination has been performed as a part of this study.

(I)

The structural base of (I) is a two-dimensional network structure of composition MnNi(CN)$_4$. The network is formed

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Figure 1
View of the crystal structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. [Symmetry codes: (i) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $x + \frac{1}{2}, y + \frac{1}{2}, z + 1$; (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$.]

with linkages of cyanide between the equatorial coordination sites of octahedral Mn^{II} ions (site symmetry $2/m$) and those of square-planar Ni^{II} ions (site symmetry $2/m$). The coordination of pyridine ligands to the axial sites of the Mn^{II} ions completes the Mn(py)$_2$Ni(CN)$_4$ complex. The crystal structure of (I) is a layered structure of the Mn(py)$_2$Ni(CN)$_4$ complex, stacking along the a axis, as shown in Fig. 1. The pyridine ligands protrude from both sides of the network plane and the aromatic rings of all pyridines are on mirror planes parallel to the ac plane. Among the Hofmann pyridine complexes, the crystal structures of Cd(py)$_2$Ni(CN)$_4$ (Ülkü, 1975) and Fe(py)$_2$Ni(CN)$_4$ (Kitazawa *et al.*, 1996) are already known. Our X-ray crystallographic analysis confirmed that these two complexes and (I) are isomorphous.

The magnetic measurement of (I) showed no significant magnetic interaction between the Mn^{II} ions. The effective magnetic moment observed was constant above 20 K. The observed value, 5.89 (1) μ_B, suggested that the Mn^{II} ions are in the high-spin state. The Weiss and Curie constants obtained from fitting to the Curie–Weiss law were −0.01 (8) K and 4.33 (1) emu K mol^{-1}, respectively.

Experimental

To 50 ml of water, MnCl$_2$·4H$_2$O (0.99 g, 5.00 mmol) and K$_2$[Ni(CN)$_4$]·H$_2$O (1.29 g, 5.00 mmol) were added with stirring, forming a white precipitate. After adding 1 g of citric acid monohydrate to the mixture, 2-aminoethanol was also added dropwise until the precipitate disappeared and the mixture turned into a pale-yellow solution of pH 7.0. The solution was filtered and the filtrate was exposed to pyridine vapour at atmospheric pressure and ordinary temperature. After several days, pale-yellow crystals of Mn(py)$_2$Ni(CN)$_4$ were obtained. Analysis calculated for C$_{14}$H$_{10}$MnN$_6$Ni: C 44.73, H 2.68, N 22.36%; found: C 42.89, H 2.76, N 21.94%. The magnetic susceptibility was measured on a Quantum Design MPMS-5 SQUID magnetometer under an applied magnetic field of 1000 Oe in

the temperature range 5–300 K. Diamagnetic corrections were made using Pascal's constants.

Crystal data

[MnNi(CN)$_4$(C$_5$H$_5$N)$_2$]	$Z = 2$
$M_r = 375.93$	$D_x = 1.563$ Mg m^{-3}
Monoclinic, $C2/m$	Mo $K\alpha$ radiation
$a = 15.684$ (8) Å	$\mu = 1.97$ mm^{-1}
$b = 7.459$ (3) Å	$T = 153$ (2) K
$c = 7.067$ (4) Å	Block, pale yellow
$\beta = 104.93$ (2)°	$0.21 \times 0.20 \times 0.12$ mm
$V = 798.8$ (7) Å^3	

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer	8928 measured reflections
	1518 independent reflections
ω scans	1246 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.028$
$T_{min} = 0.586$, $T_{max} = 0.789$	$\theta_{max} = 32.6°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 28.8858P]$
$R[F^2 > 2\sigma(F^2)] = 0.078$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.239$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.22$	$\Delta\rho_{max} = 1.02$ e Å^{-3}
1518 reflections	$\Delta\rho_{min} = -0.84$ e Å^{-3}
63 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ni1—C1	1.869 (6)	Mn1—N11	2.271 (8)
Mn1—N1	2.220 (5)	N1—C1	1.145 (8)
Ni1—C1—N1	176.2 (6)	N1—Mn1—N11	91.1 (2)
C1—Ni1—C1^i	90.0 (3)	N1—Mn1—N11^{ii}	88.9 (2)
N1—Mn1—N1^{ii}	90.0 (3)	Mn1—N1—C1	160.1 (6)

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

H atoms were placed in idealized positions and refined as riding, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The highest peak of residual electron density is located 1.58 Å from H13.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *PLATON* (Spek, 2003).

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