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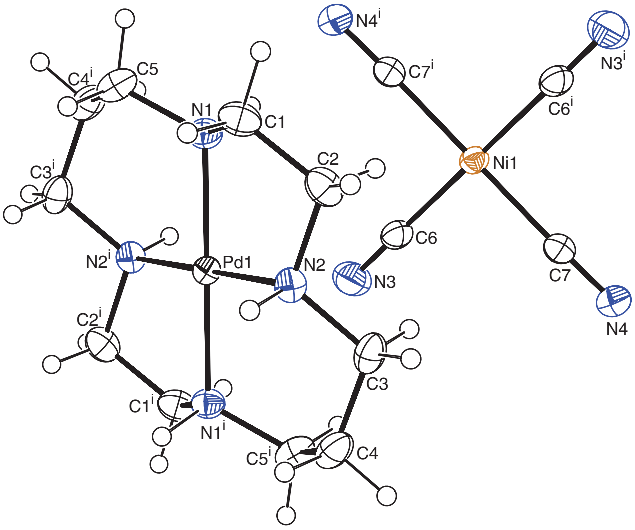
Crystal structure of (1,4,8,11-tetraazacyclotetradecane-κ^4*N*,*N′*,*N′′*,*N′′′*) palladium(II) tetracyanonickelate(II), $C_{14}H_{24}N_8NiPd$



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Abstract

$C_{14}H_{24}N_8NiPd$, monoclinic, $P2_1/n$ (no. 14), $a = 8.9786(9)$ Å, $b = 8.3191(9)$ Å, $c = 11.9489(12)$ Å, $\beta = 94.772(3)°$, $V = 889.42(16)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0161$, $wR_{ref}(F^2) = 0.0401$, $T = 223(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a solution of (1,4,8,11-tetraazacyclotetradecane) palladium(II) dichloride (0.1237 g, 0.328 mmol) in H_2O (10 mL) was added $K_2Ni(CN)_4·xH_2O$ (0.1097 g; 0.455 mmol in anhydrous basis) and refluxed for 1 h. After cooling, the formed precipitate was separated by filtration, washed with H_2O and acetone, and dried at 50 °C, to give a pale yellow powder (0.0765 g). Crystals suitable for X-ray diffraction were obtained by slow evaporation from an H_2O/dimethyl sulfoxide (DMSO) solution at 90 °C.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.16 × 0.12 × 0.04 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	2.08 mm^{-1}
Diffractometer, scan mode:	PHOTON 100 CMOS, φ and ω
θ_{max}, completeness:	26.1°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	22001, 1744, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1560
$N(param)_{refined}$:	112
Programs:	Bruker [1], SHELX [2], ORTEP-3 [3], PLATON [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	$U_{iso}*/U_{eq}$
Pd1	0.5000	0.5000	0.0000	0.02139(7)
N1	0.41795(16)	0.33776(18)	−0.11727(12)	0.0284(3)
H1	0.3156	0.3733	−0.1432	0.034*
N2	0.44102(16)	0.33423(17)	0.11395(11)	0.0269(3)
H2	0.5332	0.2763	0.1414	0.032*
C1	0.4030(2)	0.1818(2)	−0.05848(16)	0.0359(4)
H1A	0.5006	0.1291	−0.0464	0.043*
H1B	0.3353	0.1103	−0.1038	0.043*
C2	0.3413(2)	0.2158(2)	0.05258(16)	0.0351(4)
H2A	0.2399	0.2593	0.0404	0.042*
H2B	0.3374	0.1165	0.0963	0.042*
C3	0.3755(2)	0.4014(2)	0.21371(15)	0.0348(4)
H3A	0.3525	0.3134	0.2640	0.042*
H3B	0.2817	0.4564	0.1898	0.042*
C4	0.4807(2)	0.5185(2)	0.27674(16)	0.0384(5)
H4A	0.5793	0.4679	0.2891	0.046*
H4B	0.4444	0.5386	0.3506	0.046*
C5	0.5015(2)	0.3217(2)	−0.21876(15)	0.0382(4)
H5A	0.4484	0.2468	−0.2714	0.046*
H5B	0.6005	0.2765	−0.1972	0.046*
Ni1	0.0000	0.5000	0.0000	0.02491(8)
N3	0.2140(2)	0.7799(3)	0.00057(15)	0.0485(5)
N4	−0.09581(18)	0.6054(2)	0.22392(13)	0.0368(4)
C6	0.1330(2)	0.6736(2)	−0.00001(14)	0.0325(4)
C7	−0.05582(19)	0.5641(2)	0.14010(15)	0.0284(4)

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Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.98 Å, d(N—H) = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$ with the help of the SHELXL program (AFIX 23 or 13 options) [2]. The highest peak (0.31 e Å^{-3}) and the deepest hole (−0.34 e Å^{-3}) in the difference Fourier map are located 0.69 Å and 0.74 Å from atoms N1 and Pd1, respectively.

Comment

The crystal structures of the related heterometallic complexes $[Ag(cyclam)M1(CN)_4]_n$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; M1 = Pd, Pt) [5] and $[Cu(cyclam)M2(CN)_4]_n$ (M2 = Ni, Pd, Pt) [6] have been determined previously. The structures are formed by one-dimensional cyanido-bridged chains.

The title compound consists of a cationic Pd(II) complex $[Pd(cyclam)]^{2+}$ and an anionic Ni(II) complex $[Ni(CN)_4]^{2-}$. The title structure is isostructural with the previously reported cyanido-Pd complex $[Pd(cyclam)][Pd(CN)_4]$ [7]. Pd(II) and Ni(II) ions are four-coordinated in a slightly distorted square-planar environment and are located on an inversion center, respectively, and thus the asymmetric unit contains one half of the compound. In the cationic complex, the Pd(II) ion is coordinated by four N atoms from the tetradentate cyclam ligand, whereas in the anionic complex, the Ni(II) ion is coordinated by four C atoms from four CN^- ligands. In the crystal structure, the cationic and anionic complexes are linked by intermolecular N—H···N4(cyanido) hydrogen bonds with d(N···N) = 2.977(2)–3.098(2) Å, forming a three-dimensional network [4]. In the reported heterometallic complexes, the metal ions (Ag, Cu) are coordinated by different bridging cyanido ligands in axial positions with d(Ag—N) = 2.567(9) Å in Pd complex and 2.529(9) Å in Pt complex [5], and d(Cu—N) = 2.5321(9) Å in Ni complex, 2.518(2) Å in Pd complex and 2.549(3) Å in Pt complex [6], respectively. In the title compound, on the contrary, such a cyanido-bridging is not observed: the distance between the Pd1 and N3(cyanido) atoms is relatively long with 3.467(2) Å [4].

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