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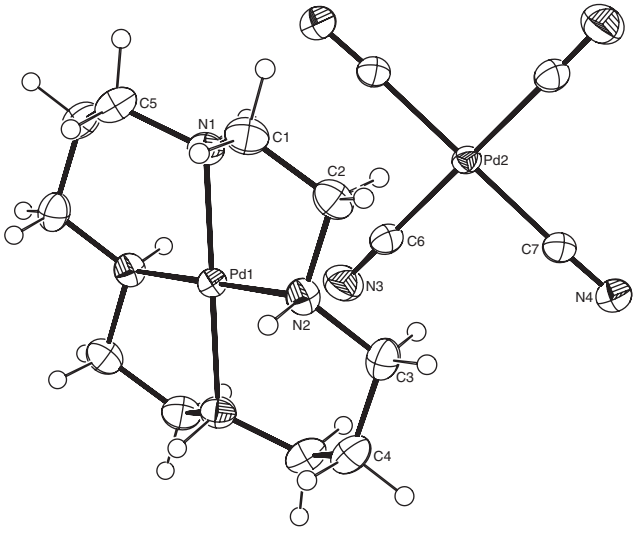
Crystal structure of (1,4,8,11-tetraazacyclotetradecane)palladium(II) tetracyanopalladate(II), $C_{14}H_{24}N_8Pd_2$



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Abstract

$C_{14}H_{24}N_8Pd_2$, monoclinic, $P2_1/n$ (no. 14), $a = 9.075(2)$ Å, $b = 8.3534(19)$ Å, $c = 12.106(3)$ Å, $\beta = 94.895(4)°$, $V = 914.3(4)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0220$, $wR_{ref}(F^2) = 0.0654$, $T = 223(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a 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 (0.2243 g, 0.594 mmol) in MeOH (10 mL)/H_2O

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.27 × 0.17 × 0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	19.8 cm^{-1}
Diffractometer, scan mode:	PHOTON 100 CMOS, φ and ω
$2\theta_{max}$, completeness:	56.8°, >95%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11356, 2185, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1591
$N(param)_{refined}$:	112
Programs:	Bruker programs [3], SHELX [4], Platon [5, 6]

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	0.02365(9)
N1	0.41976(16)	0.33760(17)	−0.11655(12)	0.0334(3)
H1	0.3186	0.3731	−0.1427	0.040*
N2	0.44116(16)	0.33414(17)	0.11241(11)	0.0319(3)
H2	0.5324	0.2765	0.1398	0.038*
C1	0.4039(2)	0.1821(2)	−0.05828(16)	0.0405(5)
H1A	0.5003	0.1292	−0.0461	0.049*
H1B	0.3367	0.1114	−0.1032	0.049*
C2	0.3427(2)	0.2161(2)	0.05134(16)	0.0391(4)
H2A	0.2422	0.2594	0.0390	0.047*
H2B	0.3386	0.1172	0.0945	0.047*
C3	0.3758(2)	0.4014(2)	0.21109(15)	0.0400(5)
H3A	0.3531	0.3138	0.2607	0.048*
H3B	0.2829	0.4559	0.1871	0.048*
C4	0.4792(3)	0.5185(2)	0.27367(17)	0.0440(5)
H4A	0.5768	0.4683	0.2867	0.053*
H4B	0.4426	0.5388	0.3462	0.053*
C5	0.5027(2)	0.3223(2)	−0.21621(15)	0.0430(5)
H5A	0.4504	0.2477	−0.2683	0.052*
H5B	0.6007	0.2773	−0.1946	0.052*
Pd2	0.0000	0.5000	0.0000	0.02629(9)
N3	0.2167(2)	0.7952(2)	0.00124(14)	0.0551(5)
N4	−0.10158(19)	0.6085(2)	0.23003(13)	0.0420(4)
C6	0.1380(2)	0.6877(2)	0.00010(14)	0.0373(4)
C7	−0.0606(2)	0.5671(2)	0.14771(15)	0.0329(4)

(10 mL) was added $K_2Pd(CN)_4 \cdot xH_2O$ (0.1742 g; 0.603 mmol in anhydrous basis) and stirred for 10 min at room temperature. The formed precipitate was separated by filtration, washed with H_2O and MeOH, and dried at 50 °C, to give a white powder (0.0908 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an *N,N*-dimethylformamide/H_2O solution at 60 °C.

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). The highest peak (0.23 e Å^{-3}) and the deepest hole (−0.69 e Å^{-3}) in the difference Fourier map are located 0.41 Å and 0.42 Å from the atoms N1 and Pd2, respectively.

Discussion

The crystal structures of the related heterometallic complexes [M(cyclam)Pd(CN)$_4$] (cyclam = 1,4,8,11-tetraazacyclotetradecane; M = Ag, Cu) have been determined previously [1, 2]. The structures are formed by one-dimensional cyanido-bridged chains exhibiting [—M(cyclam)—NC—Pd(CN)$_2$—CN—]$_n$ composition.

The title compound consists of a cationic Pd(II) complex [Pd(cyclam)]$^{2+}$ and an anionic Pd(II) complex [Pd(CN)$_4$]$^{2-}$. Each Pd(II) ion is four-coordinated in a slightly distorted square-planar environment and is located on an inversion center, and thus the asymmetric unit contains one half of each ion. 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 Pd(II) ion is coordinated by four C atoms from four CN^- ligands. The Pd—N and Pd—C bond lengths are almost equal with (d(Pd—N) = 2.0447(14)–2.0459(14) Å and d(Pd—C) = 1.9955(19)–2.007(2) Å), respectively. In the crystal structure, the cationic and anionic complexes are linked by intermolecular N—H···N4(cyanido) hydrogen bonds with d(N···N) = 2.973(2)–3.123(2) Å, forming a three-dimensional network. 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 [1] and d(Cu—N) = 2.518(2) Å [2], respectively. In the title compound, on the contrary, such a cyanido-bridging is not observed: the distance between the Pd1 and N3 atoms is relatively long with 3.563(2) Å.

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