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Crystal structure of *cyclo*[tetra(μ_2 -cyanido)-tetracyanido-bis(1,4,7,10-tetraazacyclododecane- κ^4N,N',N'',N''')dinickel(II)dipalladium(II)] hexahydrate, $C_{24}H_{52}N_{16}Ni_2O_6Pd_2$

Table 1: Data collection and handling.

Crystal:	Purple rod
Size:	0.20 × 0.15 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.96 mm ⁻¹
Diffractometer, scan mode:	PHOTON 100 CMOS, φ and ω
$\theta_{\max}$, completeness:	26.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	51951, 3786, 0.039
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3419
$N(\text{param})_{\text{refined}}$:	226
Programs:	Bruker [1], SHELX [2], ORTEP-3 [3], PLATON [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd1	0.86507(3)	0.57290(2)	0.42425(2)	0.02344(10)
Ni1	0.50742(4)	0.28563(3)	0.36438(3)	0.01641(11)
N1	0.3688(3)	0.16644(19)	0.35914(18)	0.0227(6)
H1	0.3031	0.1694	0.4088	0.027*
N2	0.3430(3)	0.3350(2)	0.26613(19)	0.0254(6)
H2	0.3100	0.3995	0.2802	0.030*
N3	0.6291(3)	0.2550(2)	0.25602(19)	0.0255(6)
H3	0.5887	0.1955	0.2303	0.031*
N4	0.6761(3)	0.1908(2)	0.42167(19)	0.0266(6)
H4	0.7245	0.2187	0.4753	0.032*
N5	0.6426(3)	0.4039(2)	0.3880(2)	0.0273(6)
N6	0.3761(3)	0.3316(2)	0.4640(2)	0.0278(6)
N7	1.0757(4)	0.7496(3)	0.4377(2)	0.0442(9)
N8	1.0824(5)	0.4854(3)	0.2955(3)	0.0476(9)
C1	0.2639(4)	0.1695(3)	0.2803(2)	0.0324(8)
H1A	0.1752	0.1277	0.2863	0.039*
H1B	0.3188	0.1490	0.2305	0.039*
C2	0.2087(4)	0.2702(3)	0.2678(3)	0.0331(8)
H2A	0.1449	0.2753	0.2135	0.040*
H2B	0.1446	0.2879	0.3148	0.040*
C3	0.4154(5)	0.3355(3)	0.1821(2)	0.0348(9)
H3A	0.3855	0.3929	0.1503	0.042*
H3B	0.3780	0.2815	0.1476	0.042*
C4	0.5914(5)	0.3310(3)	0.1963(3)	0.0416(10)
H4A	0.6380	0.3194	0.1415	0.050*
H4B	0.6317	0.3906	0.2201	0.050*
C5	0.7898(5)	0.2408(3)	0.2877(3)	0.0400(10)
H5A	0.8351	0.3008	0.3075	0.048*
H5B	0.8499	0.2171	0.2410	0.048*
C6	0.7973(4)	0.1723(3)	0.3600(3)	0.0373(9)
H6A	0.8999	0.1757	0.3907	0.045*

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Abstract

$C_{24}H_{52}N_{16}Ni_2O_6Pd_2$, monoclinic, $P2_1/c$ (no. 14), $a = 8.6416(3)$ Å, $b = 14.2237(5)$ Å, $c = 15.5573(5)$ Å, $\beta = 93.8054(12)^\circ$, $V = 1908.02(11)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0312$, $wR_{\text{ref}}(F^2) = 0.0915$, $T = 223(2)$ K.

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The molecular structure is shown in the figure (Only the asymmetric unit is labelled). 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 $K_2Pd(CN)_4 \cdot xH_2O$ (0.1191 g; 0.413 mmol in anhydrous basis) in H_2O (20 mL) were added 1,4,7,10-tetraazacyclododecane-4HCl (0.1028 g, 0.323 mmol) and $Ni(CH_3CO_2)_2 \cdot 4H_2O$ (0.0856 g, 0.344 mmol), followed by

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H6B	0.7837	0.1086	0.3368	0.045*
C7	0.5901(5)	0.1045(3)	0.4424(3)	0.0359(9)
H7A	0.5409	0.1133	0.4968	0.043*
H7B	0.6625	0.0516	0.4495	0.043*
C8	0.4669(5)	0.0825(2)	0.3709(3)	0.0308(8)
H8A	0.5155	0.0675	0.3174	0.037*
H8B	0.4045	0.0284	0.3868	0.037*
C9	0.7241(4)	0.4652(2)	0.4044(2)	0.0233(7)
C10	0.2862(4)	0.3665(2)	0.5039(2)	0.0231(7)
C11	1.0005(4)	0.6835(3)	0.4363(2)	0.0280(8)
C12	1.0065(4)	0.5157(3)	0.3459(3)	0.0295(8)
O1	0.1713(4)	0.0869(3)	0.4848(3)	0.0646(10)
H11	0.0990	0.0865	0.5183	0.097*
H12	0.1316	0.0445	0.4528	0.097*
O2	0.6062(5)	0.0786(4)	0.1519(3)	0.0975(19)
H21	0.6979	0.0613	0.1462	0.146*
H22	0.5441	0.0419	0.1250	0.146*
O3	0.9449(8)	0.4401(3)	0.1203(3)	0.1043(19)
H31	0.9269	0.3822	0.1232	0.156*
H32	0.9596	0.4473	0.1738	0.156*

refluxing for 3 h. After cooling, the formed precipitate was separated by filtration, washed with H₂O and acetone, and dried at 50 °C, to give a pale blue powder (0.1282 g). From the filtrate and washing solution was obtained a small amount of a purple powder. Purple crystals suitable were obtained by the slow evaporation from H₂O 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 $U_{iso}(H) = 1.2U_{eq}(C, N)$ with the help of the SHELXL program (AFIX 23 or 13 options) [2]. The H atoms of the solvent water molecules were located from difference maps then allowed to ride on their parent O atom in the final cycles of refinement with $d(O-H) = 0.84$ Å. The highest peak (1.18 e Å⁻³) and the deepest hole (−0.52 e Å⁻³) in the difference Fourier map are located 0.27 Å and 0.49 Å from the atoms Ni1 and Pd1, respectively.

Comment

The crystal structures of the related cyanido-bridged complexes [(cyclen)Ni(μ₂-NC)₂M(CN)₂]₂·6H₂O (cyclen = 1, 4, 7, 10-tetraazacyclododecane; M = Pt, Ni) and [(cyclen)Mn(μ₂-NC)₂Ni(CN)₂]₂·6H₂O have been determined previously [5].

The title complex has a cyclic tetranuclear structure, in which four *cis*-cyanido ligands of two Pd(II) units [Pd(CN)₄]^{2−} are linked to two Ni(II) units [Ni(cyclen)]²⁺, and is isostructural with the previously reported complexes. In the complex, each Pd(II) ion is coordinated in a slightly distorted square-planar environment by four C atoms from four CN[−] ligands, whereas each Ni(II) ion is six-coordinated in a distorted octahedral coordination geometry by four N atoms of a tetradentate cyclen ligand and two N atoms derived from two mutually *cis*-positioned bridging CN[−] ligands. The linking of two Pd units and two Ni units forms a slightly puckered 12-membered square structure, and an inversion center is located at the center of the square; the asymmetric unit contains one half of the compound. The Pd–C and C≡N bond lengths are almost equal with $d(Pd-C) = 1.960(4)–1.973(3)$ Å and $d(C≡N) = 1.139(5)–1.143(5)$ Å, respectively. Two of the Ni–N(cyclen) bonds [Ni1–N2/4 = 2.135(3) and 2.137(3) Å] are slightly longer than the other Ni–N(cyclen) bonds [Ni1–N1/3 = 2.074(3) and 2.091(3) Å] and the Ni–N(cyanido) bonds [Ni1–N5/6 = 2.067(3) and 2.086(3) Å]. In the crystal structure, the complex and solvent water molecules are linked by extensive intermolecular N–H...O, N–H...N, O–H...O and O–H...N hydrogen bonds with distances of 2.796(7)–3.318(5) Å between the donor and acceptor atoms, forming a three-dimensional network [4].

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