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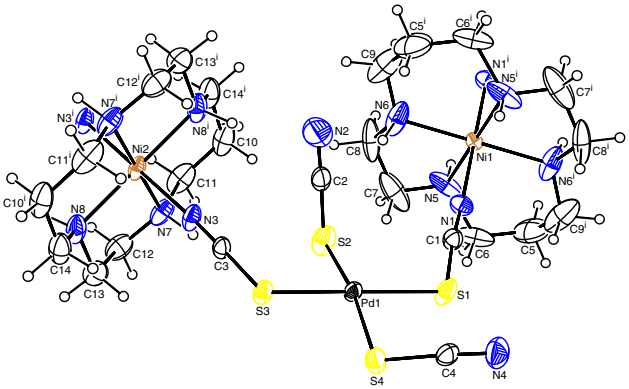
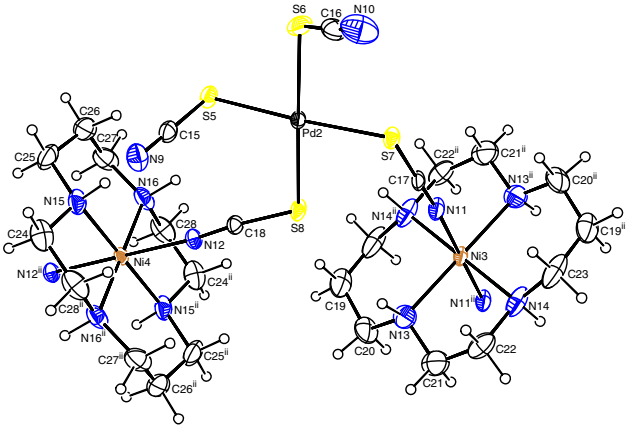
Crystal structure of *catena*-poly [(1,4,8,11-tetraazacyclotetradecane-κ^4N,N',N'',N''')-bis(μ_2-thiocyanato-$\kappa^2N:S$)-bis(thiocyanato-κS)-nickel(II)palladium(II)], $C_{14}H_{24}N_8NiPdS_4$





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Abstract

$C_{14}H_{24}N_8NiPdS_4$, triclinic, $P\bar{1}$ (no. 2), a = 12.0330(8) Å, b = 12.0959(8) Å, c = 15.9551(12) Å, α = 85.768(3)°, β = 71.917(3)°, γ = 87.899(3)°, V = 2201.3(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0379, $wR_{ref}(F^2)$ = 0.0973, T = 223 K.

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Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.20 × 0.12 × 0.10 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	2.07 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}:	56699, 8670, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 7640
$N(param)_{refined}$:	511
Programs:	Bruker [1], SHELX [2], ORTEP-3 [3], PLATON [4]

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 [Ni(NCS)$_2$(cyclam)] (cyclam = 1,4,8,11-tetraazacyclotetradecane; 0.2229 g, 0.594 mmol) in acetone (20 ml) was added $K_2Pd(SCN)_4$ (0.2501 g, 0.600 mmol) and refluxed for 2 h. After cooling, the formed precipitate was separated by filtration, washed with acetone, and dried at 50 °C, to give a redbrown powder (0.1815 g). Crystals were obtained by slow evaporation from an *N*,*N*-dimethylformamide (DMF) 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,

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.40991 (3)	0.01828 (3)	0.65109 (2)	0.03873 (10)
Ni1	0.5000	0.5000	0.5000	0.02997 (15)
Ni2	0.0000	0.0000	0.5000	0.04070 (19)
S1	0.55706 (14)	0.13849 (12)	0.64671 (14)	0.0757 (5)
S2	0.36764 (14)	0.11266 (14)	0.53229 (11)	0.0680 (4)
S3	0.25772 (11)	−0.10661 (10)	0.68036 (9)	0.0500 (3)
S4	0.46462 (16)	−0.10186 (11)	0.75464 (12)	0.0691 (5)
N1	0.5270 (4)	0.3424 (3)	0.5598 (3)	0.0460 (9)
N2	0.1732 (7)	0.2397 (5)	0.6196 (5)	0.100 (2)
N3	0.1097 (4)	−0.0405 (3)	0.5801 (3)	0.0492 (10)
N4	0.5779 (5)	0.0179 (5)	0.8466 (4)	0.0743 (15)
N5	0.5838 (6)	0.4486 (4)	0.3767 (3)	0.0788 (18)
H5	0.5887	0.5144	0.3350	0.095*
N6	0.3524 (5)	0.4390 (5)	0.4835 (4)	0.0820 (19)
H6	0.3396	0.3658	0.5168	0.098*
N7	0.1470 (4)	0.0048 (4)	0.3892 (3)	0.0617 (12)
H7	0.2160	−0.0004	0.4106	0.074*
N8	−0.0032 (4)	−0.1667 (4)	0.4780 (3)	0.0628 (13)
H8	−0.0622	−0.1739	0.4471	0.075*
C1	0.5361 (4)	0.2574 (4)	0.5932 (3)	0.0439 (10)
C2	0.2567 (6)	0.1864 (4)	0.5834 (4)	0.0609 (15)
C3	0.1734 (4)	−0.0651 (4)	0.6187 (3)	0.0398 (10)
C4	0.5310 (4)	−0.0282 (4)	0.8078 (3)	0.0481 (11)
C5	0.7838 (7)	0.4833 (8)	0.3923 (7)	0.116 (3)
H5A	0.7812	0.5553	0.3604	0.139*
H5B	0.8651	0.4566	0.3727	0.139*
C6	0.7133 (7)	0.4062 (6)	0.3633 (5)	0.090 (3)
H6A	0.7116	0.3344	0.3964	0.108*
H6B	0.7510	0.3947	0.3006	0.108*
C7	0.5179 (11)	0.3739 (6)	0.3550 (5)	0.118 (4)
H7A	0.5254	0.3008	0.3838	0.142*
H7B	0.5436	0.3675	0.2909	0.142*
C8	0.3912 (9)	0.4152 (7)	0.3862 (5)	0.102 (3)
H8A	0.3830	0.4830	0.3509	0.122*
H8B	0.3403	0.3591	0.3768	0.122*
C9	0.2464 (7)	0.4975 (9)	0.5125 (7)	0.117 (4)
H9A	0.1842	0.4554	0.5025	0.141*
H9B	0.2523	0.5689	0.4783	0.141*
C10	0.1507 (6)	0.2125 (6)	0.3812 (4)	0.076 (2)
H10A	0.2071	0.2036	0.4144	0.091*
H10B	0.1765	0.2752	0.3376	0.091*
C11	0.1584 (5)	0.1094 (6)	0.3312 (4)	0.076 (2)
H11A	0.0965	0.1127	0.3032	0.091*
H11B	0.2337	0.1081	0.2843	0.091*
C12	0.1461 (6)	−0.0947 (6)	0.3457 (4)	0.0720 (17)
H12A	0.2237	−0.1083	0.3040	0.086*
H12B	0.0898	−0.0865	0.3124	0.086*
C13	0.1129 (6)	−0.1908 (6)	0.4133 (4)	0.0712 (16)
H13A	0.1090	−0.2585	0.3842	0.085*
H13B	0.1719	−0.2022	0.4440	0.085*
C14	−0.0365 (6)	−0.2434 (5)	0.5565 (5)	0.0748 (19)
H14A	0.0235	−0.2436	0.5863	0.090*
H14B	−0.0406	−0.3185	0.5386	0.090*

Table 2: (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Pd2	0.93554 (2)	0.44721 (2)	0.12721 (2)	0.02725 (8)
Ni3	1.0000	0.0000	0.0000	0.03090 (16)
Ni4	0.5000	0.5000	0.0000	0.02828 (15)
S5	0.85268 (10)	0.59981 (9)	0.06996 (7)	0.0390 (2)
S6	1.05965 (12)	0.57290 (10)	0.15527 (10)	0.0545 (3)
S7	1.02674 (9)	0.30026 (8)	0.18631 (7)	0.0362 (2)
S8	0.81388 (10)	0.31918 (9)	0.09892 (9)	0.0461 (3)
N9	0.6479 (4)	0.6245 (4)	0.2142 (3)	0.0551 (11)
N10	1.0935 (5)	0.4998 (6)	0.3169 (4)	0.0837 (17)
N11	1.0144 (3)	0.1220 (3)	0.0859 (3)	0.0404 (8)
N12	0.6275 (3)	0.4230 (3)	0.0522 (2)	0.0366 (8)
N13	0.8194 (4)	0.0037 (4)	0.0536 (3)	0.0624 (12)
H13	0.7995	0.0645	0.0942	0.075*
N14	0.9957 (5)	−0.1255 (3)	0.0958 (3)	0.0618 (13)
H14	1.0071	−0.1963	0.0665	0.074*
N15	0.5137 (4)	0.6438 (3)	0.0586 (3)	0.0499 (10)
H15	0.5794	0.6309	0.0832	0.060*
N16	0.6323 (3)	0.5413 (4)	−0.1154 (3)	0.0522 (11)
H16	0.7071	0.5218	−0.1039	0.063*
C15	0.7333 (4)	0.6139 (3)	0.1573 (3)	0.0385 (9)
C16	1.0765 (4)	0.5283 (4)	0.2521 (4)	0.0506 (12)
C17	1.0189 (3)	0.1950 (3)	0.1267 (3)	0.0305 (8)
C18	0.7058 (3)	0.3851 (3)	0.0710 (3)	0.0314 (8)
C19	0.7951 (6)	0.1229 (5)	−0.0756 (5)	0.075 (2)
H19A	0.7869	0.1883	−0.0413	0.090*
H19B	0.7415	0.1340	−0.1110	0.090*
C20	0.7523 (6)	0.0261 (5)	−0.0115 (5)	0.0764 (19)
H20A	0.7569	−0.0400	−0.0445	0.092*
H20B	0.6699	0.0390	0.0212	0.092*
C21	0.7876 (6)	−0.0966 (5)	0.1063 (5)	0.0736 (17)
H21A	0.7883	−0.1570	0.0685	0.088*
H21B	0.7082	−0.0893	0.1471	0.088*
C22	0.8701 (6)	−0.1231 (4)	0.1570 (4)	0.0621 (15)
H22A	0.8512	−0.1954	0.1895	0.075*
H22B	0.8622	−0.0672	0.2001	0.075*
C23	1.0814 (7)	−0.1226 (4)	0.1396 (5)	0.080 (2)
H23A	1.0722	−0.1871	0.1820	0.096*
H23B	1.0691	−0.0557	0.1727	0.096*
C24	0.4094 (5)	0.6511 (5)	0.1338 (4)	0.0657 (15)
H24A	0.3438	0.6801	0.1142	0.079*
H24B	0.4222	0.7016	0.1752	0.079*
C25	0.5428 (5)	0.7474 (4)	−0.0019 (4)	0.0648 (16)
H25A	0.4755	0.7694	−0.0218	0.078*
H25B	0.5576	0.8075	0.0311	0.078*
C26	0.6469 (5)	0.7318 (5)	−0.0803 (4)	0.0665 (16)
H26A	0.6689	0.8050	−0.1104	0.080*
H26B	0.7114	0.7048	−0.0586	0.080*
C27	0.6389 (5)	0.6564 (5)	−0.1476 (4)	0.0671 (17)
H27A	0.5695	0.6765	−0.1653	0.081*
H27B	0.7076	0.6664	−0.2000	0.081*
C28	0.6179 (5)	0.4616 (6)	−0.1783 (3)	0.0629 (15)
H28A	0.5546	0.4877	−0.2016	0.075*
H28B	0.6901	0.4582	−0.2280	0.075*

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 (1.25 e Å^{-3}) and the deepest hole (–1.07 e Å^{-3}) in the difference Fourier map are located 0.99 and 0.64 Å from the atoms N13 and S2, respectively.

Comment

The crystal structures of the related heterometallic cyanido-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 two streochemically different heterometallic complexes $[Ni(cyclam)Pd(SCN)_4]_n$. In the *trans*-like complex moiety of the title coordination polymer (upper part of the Figure), two trans-thiocyanato ligands of Pd(II) unit $[Pd(SCN)_4]^{2-}$ are linked to two Ni(II) units $[Ni(cyclam)]^{2+}$, whereas in the *cis*-like complex moiety, two *cis*-coordinated thiocyanato ligands of the Pd(II) unit (lower part of the Figure) are linked to the two Ni(II) units. The both complexes moieties are connected to exhibit one-dimensional SCN-bridged chains. The Pd(II) ion in each complex is four-coordinated in a distorted square-planar environment by four S atoms from four SCN^- ligands, whereas the Ni(II) ions in each complex are six-coordinated in a distorted octahedral coordination geometry by four N atoms of a tetradentate cyclam ligand and two N atoms derived from two mutually *trans*-positioned bridging SCN^- ligands and are located on an inversion center. The Pd–S bond lengths are almost equal with d(Pd–S) = 2.3133(13)–2.3507(13) Å. The Ni–N(thiocyanato) bonds with d(Ni–N) = 2.119(3)–2.133(3) Å are slightly longer than the Ni–N(cyclam) bonds with d(Ni–N) = 2.043(4)–2.076(5) Å. In the crystal structure, the complexes display intra- and intermolecular N–H···N hydrogen bonds with distances of 2.909(6)–3.447(9) Å between the donor and acceptor atoms, to stabilize the three-dimensional packing [4].

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