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cis-Diamminedicyanopalladium(II)

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Abstract. $[Pd(CN)_2(NH_3)_2]$, $M_r = 192{\cdot}5$, monoclinic, $P2_1/n$, $a = 6{\cdot}825$ (2), $b = 12{\cdot}733$ (3), $c = 6{\cdot}779$ (2) Å, $\beta = 111{\cdot}82$ (2)°, $V = 546{\cdot}9$ (3) Å^3, $Z = 4$, $D_m = 2{\cdot}41$, $D_x = 2{\cdot}34$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 37{\cdot}6$ cm^{-1}, $F(000) = 368$, room temperature, final $R = 0{\cdot}030$ for 1414 independent observed reflections. The structure is built up of independent molecules linked together by N—H···N hydrogen bonds. The Pd atom is bonded to two NH_3 and two CN ligands in a square-planar coordination. The two ligands of each pair are *cis* to each other. The PdC_2N_2 fragment is almost planar.

Introduction. The title compound was prepared in the course of our attempts to prepare tetraammine-palladium(II) tetracyanopalladate(II) – the cyanide analogue of the Vauquelin Red Salt, $[Pd(NH_3)_4][PdCl_4]$, the successful solution and refinement of the structure showing that *cis*-diamminedicyanopalladium(II) was obtained instead. Compounds with the same overall composition have been known for a long time, Fehling (1841) describing a compound formulated as $Pd(CN)_2.2NH_3$. Later on Feigl & Heisig (1951) obtained [by warming palladium(II) cyanide in an excess of ammonia] diamminedicyanopalladium(II), Gillard (1965) claiming (on the basis of his IR results) to have studied the *trans* isomer.

Experimental. The freshly prepared equimolar aqueous solutions of $[Pd(NH_3)_4]Cl_2$ and $K_2[Pd(CN)_4]$ were mixed and left for several days. The reaction product was filtered off and recrystallized from hot water. Density determined pycnometrically. Needle-like crystals of dimensions 0·65 × 0·07 × 0·07 mm, Philips PW 1100 diffractometer, graphite monochromator, Mo $K\alpha$, ω–2θ scan technique, 18 reflections in range $6 \le \theta \le 10°$ used to determine cell parameters. Data collected within range $3 < \theta < 31°$, h −9→8, k 0→16, l 0→9, 1414 unique observed reflections used in structure determination. Three standard reflections measured every 2 h of exposure time showed no significant change with time. Data corrected for Lorentz and polarization effects but not for absorption. Atomic scattering factors and anomalous-dispersion corrections for Pd atom from *International Tables for X-ray Crystallography* (1974). Patterson map indicated position of Pd; positions of other atoms (except H) obtained by Fourier-map calculations; H-atom positions from difference Fourier synthesis; least-squares refinement (on F) assuming anisotropic thermal parameters for non-H atoms and isotropic temperature factors for all H atoms. Refinement converged with

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$R = 0{\cdot}030$ assuming unit weight for all observations. $(\Delta/\sigma)_{max} = 0{\cdot}047$. Max. and min. height in final difference Fourier map 1·36 and $-1{\cdot}5$ e Å^{-3}. All calculations performed using the Univac 1110 of the Zagreb University Computing Centre, SRCE, with programs written by Domenicano, Spagna & Vaciago (1969) and Sheldrick (1976).

IR spectra recorded on Perkin–Elmer Model 580 spectrophotometer at room and liquid-nitrogen temperature (4000–200 cm^{-1}): 3340, 3315, 3255, 3185 [ν(NH)]; 2145, 2133 [ν(CN)]; 1630, 1600 [$\delta_{as}(NH_3)$]; 1395, 1385, 1373 [$\delta_s(NH_3)$]; 810, 765, 732, 718 [$\rho(NH_3)$]; 490, 470, 420, 395 [ν(PdN)] and [ν(PdC)] (room-temperature values).

Discussion. The final atomic parameters are given in Table 1.* The interatomic distances and angles are listed in Table 2 according to the numbering scheme of Fig. 1.

The structure consists of the title molecules held together by N–H···N hydrogen bonds. The Pd atom is surrounded by two NH_3 and two CN ligands in a square-planar coordination. The two ligands of each pair are *cis* to each other. The angles at the Pd atom range from 87·7 (2) to 91·7 (2)°. The PdC_2N_2 fragment is almost planar, the deviations from the least-squares best plane through the two C and two N atoms are: Pd −0·006, C(1) 0·009, C(2) −0·009, N(1) 0·008 and N(2) −0·008 Å, respectively. The bonds Pd–C≡N are essentially collinear with the angles at the C atom 178·0 (5) and 179·7 (3)°. The Pd–C, Pd–N and C≡N bond lengths with the mean values of 1·958 (8), 2·084 (7) and 1·139 (10) Å are within the expected ranges.

The Pd···Pd contact between centrosymmetrical pairs is 3·340 (1) Å, which suggests a weak interaction between two Pd atoms (Jeitschko, 1974).

Considering intermolecular contacts less than 3·5 Å there are seven possible hydrogen bonds between N atoms from NH_3 and CN ligands (Pimentel & McClellan, 1960). Two of them, N(1)–H(11)···N(21^{i})(−x, −y, −1−z) and N(2)–H(21)···N(11^{ii})($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$), are significantly shorter amounting to 3·150 (6) and 3·049 (7) Å, respectively.

The IR spectra are in agreement with the structure and show some interesting features which are discussed elsewhere (Šoptrajanova, Šoptrajanov & Jovanovski, 1986).

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* Lists of structure factors, atomic coordinates and isotropic thermal parameters for H atoms and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42982 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic temperature factors for non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = \sum_i \sum_j b_{ij}(\mathbf{a}_i.\mathbf{a}_j)/6\pi^2$.

	x	y	z	U_{eq}(Å^2 × 10^4)
Pd	2480 (1)	−138·0 (3)	136 (1)	229 (1)
C(1)	3455 (8)	1211 (4)	1580 (8)	287 (17)
C(2)	2120 (8)	570 (4)	−2526 (9)	290 (16)
N(1)	1491 (8)	−1573 (4)	−1425 (8)	327 (15)
N(2)	2900 (8)	−837 (4)	3029 (8)	324 (16)
N(11)	4034 (8)	1973 (4)	2466 (9)	414 (19)
N(21)	1899 (9)	983 (4)	−4093 (8)	397 (18)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Pd–C(1)	1·966 (5)	N(1)–H(11)	0·93 (7)
Pd–C(2)	1·949 (6)	N(1)–H(12)	1·10 (10)
Pd–N(1)	2·093 (5)	N(1)–H(13)	0·81 (11)
Pd–N(2)	2·075 (5)	N(2)–H(21)	0·83 (8)
C(1)–N(11)	1·133 (7)	N(2)–H(22)	0·91 (8)
C(2)–N(21)	1·144 (7)	N(2)–H(23)	0·89 (8)
C(1)–Pd–C(2)	87·7 (2)	H(11)–N(1)–H(12)	94 (6)
N(1)–Pd–N(2)	90·5 (2)	H(11)–N(1)–H(13)	81 (8)
N(1)–Pd–C(2)	91·7 (2)	H(12)–N(1)–H(13)	119 (9)
N(2)–Pd–C(1)	90·1 (2)	H(21)–N(2)–H(22)	106 (7)
N(1)–Pd–C(1)	178·9 (2)	H(21)–N(2)–H(23)	98 (6)
N(2)–Pd–C(2)	177·8 (2)	H(22)–N(2)–H(23)	116 (7)
Pd–C(1)–N(11)	178·0 (5)		
Pd–C(2)–N(21)	179·7 (3)		

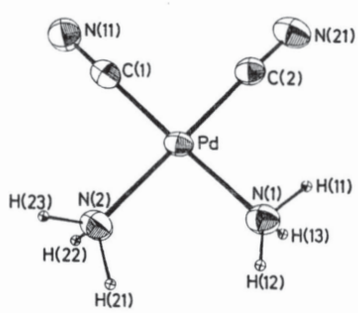

Fig. 1. Molecular conformation and atomic numbering.

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