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[1-(2-Carboxyphenyl)-3,5-diphenylformazanato](pyridine)palladium(II), [Pd(C₂₀H₁₄N₄O₂)(C₅H₅N)]

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Abstract. $M_r = 527.9$, monoclinic, $P2_1/n$, $a = 10.169$ (1), $b = 19.487$ (3), $c = 11.050$ (1) Å, $\beta = 97.52$ (2)°, $V = 2170.9$ (5) Å³, $Z = 4$, $D_x = 1.61$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 8.74$ cm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 1064$, room temperature, $R = 0.038$ for 4232 reflexions. Pd has an approximately square-planar coordination in which the terminal N atoms of the formazan moiety [Pd–N 1.969 (4) and 1.987 (4) Å], one O atom of the carboxyl group [Pd–O 2.005 (3) Å] and the pyridine N atom [Pd–N 2.081 (5) Å] are involved.

Introduction. Square-planar complexes of transition-metal d^8 ions with the bidentate dibasic 1-(2-hydroxyphenyl)-3,5-diphenylformazan are interesting model compounds for mechanistic studies on ligand-substitution reactions (Balt & Meuldijk, 1981; Balt, Meuldijk & Wismeijer, 1981). The rigidity of the formazan moiety hinders the formation of a five-coordinated intermediate which is usually formed in substitution reactions at square-planar complexes. Until now complexes of only one tridentate formazan have been reported and to investigate other tridentate formazans the title complex has been isolated.

Experimental. 1-(2-Carboxyphenyl)-3,5-diphenylformazan was prepared according to a method described by Wizinger & Biro (1949). 6 mmol of Pd(NO₃)₂·2H₂O dissolved in a minimum amount of water were added slowly to a boiling solution of 5 mmol of the formazan in 100 cm³ 96% ethanol. The reaction mixture was cooled to room temperature and the precipitate was separated by filtration and dissolved in 150 cm³ boiling trichloromethane. To this solution 25 cm³ and 150 cm³ water were added successively. The organic layer containing PDFORM was separated and filtered. 25 cm³ methanol was added to the filtrate and PDFORM crystals were formed by slow evaporation of the solvent in air. The product was dried *in vacuo* over KOH. Yield: 67%. Analysis (%): calculated for C₂₅H₁₉N₅O₂Pd: Pd, 20.16; C, 56.89; H, 3.63; found: Pd, 19.84; C, 55.90; H, 3.64.

D_m not measured. 33 reflexions (2θ 41–56°) used to measure lattice parameters; $2\theta_{\text{max}} = 60^\circ$, $h - 14$ to 14, $k 0$ to 27, $l 0$ to 15; one standard reflexion, no systematic variation; 6297 unique reflexions, 4232 with $I > 2.5\sigma(I)$; Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation; no absorption correction (crystal dimensions 0.10 × 0.10 × 0.15 mm). Structure solved by means of a Patterson minimum function based on the four Pd atoms in the unit cell. Refinement on F proceeded by anisotropic block-diagonal least-squares calculations during the course of which a ΔF synthesis indicated the H atoms,

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which were refined isotropically. Anomalous dispersion of Pd taken into account and weighting scheme $w = (1 + F_o + 0.165F_o^2)^{-1}$ was used; $wR = 0.082$; $(\Delta/\sigma)_{\max} = 0.65$; $(\Delta\rho)_{\max} = 0.8$, $(\Delta\rho)_{\min} = -0.3 \text{ e } \text{Å}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974); no correction for extinction. Calculations performed with the *XRAY76* system (Stewart, 1976) and a local program for the Patterson minimum function.

Discussion. Final atomic parameters are given in Table 1.* The shape of the molecule and the atomic numbering are indicated in Fig. 1. The Pd atom has an approximately square-planar coordination with small out-of-plane deviations of 0.02 Å (Fig. 2). There is a clear difference between the Pd–N distances to the formazan N atoms (1.97 and 1.99 Å) and to the pyridine N atom (2.08 Å) as in the corresponding Ni complex (1.82, 1.83 and 1.93 Å respectively) (Meuldijk, Renkema, van Herk & Stam, 1983). The six-membered ring PdN(1)N(2)C(3)N(4)N(5) is boat shaped with folding angles of 21.4 and 12.0° about N(1)–N(5) and N(2)–N(4) respectively. The part N(1)N(2)N(4)N(5) is planar within 0.007 Å. The four aromatic rings C(6)–C(11), C(15)–C(20), C(21)–C(26) and N(27)–C(32) have largest deviations from planarity of 0.030, 0.011, 0.011 and 0.012 Å respectively and make angles of 37, 11, 41 and 29° respectively with the best plane of the formazan nucleus. There are considerable differences from the related complex bis(1,3,5-tri-*p*-tolylformazan)Pd (TTFPd) (Siedle & Pignolet, 1980) in which Pd is squarely coordinated to two formazan moieties. The average Pd–N distance in TTFPd is 2.024 Å against 1.978 Å (to formazan N) in PDFORM. The N–Pd–N angle within the Pd–formazan ring is 80.4° in TTFPd against 87.4° in PDFORM, and the folding of the Pd–formazan ring is more pronounced in TTFPd than in PDFORM [folding angles about N(1)–N(5) 43.2 and 21.4°, about N(2)–N(4) 21.6 and 12.0° respectively]. In Table 2 a comparison is made of bond lengths and angles of the formazan moieties in PDFORM, NIFORM (Meuldijk *et al.*, 1983), CUFORM (Renkema *et al.*, 1979) and TTFPd. The bond lengths within the formazan nuclei are in reasonable agreement; the bond angles show a somewhat larger variation. The lengths of the bonds to the attached phenyl rings show a variation which is correlated with the angle between the ring and the plane of the formazan nucleus, the bond lengths increasing with increase of this angle.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39962 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters with calculated e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Pd	0.94552 (3)	0.03270 (2)	0.13753 (3)	0.0383 (1)
N(1)	1.0573 (3)	0.1155 (2)	0.1458 (3)	0.039 (1)
N(2)	1.1833 (3)	0.1169 (2)	0.1802 (3)	0.039 (1)
C(3)	1.2524 (4)	0.0640 (3)	0.2336 (4)	0.037 (1)
N(4)	1.2035 (4)	0.0074 (2)	0.2840 (3)	0.041 (1)
N(5)	1.0790 (4)	-0.0077 (2)	0.2651 (3)	0.040 (1)
C(6)	1.0043 (4)	0.1818 (3)	0.1139 (4)	0.039 (1)
C(7)	0.8867 (4)	0.1914 (3)	0.0318 (4)	0.043 (1)
C(8)	0.8510 (5)	0.2585 (3)	-0.0032 (6)	0.062 (2)
C(9)	0.9216 (6)	0.3144 (3)	0.0472 (7)	0.069 (2)
C(10)	1.0320 (5)	0.3056 (3)	0.1325 (6)	0.058 (2)
C(11)	1.0711 (5)	0.2390 (3)	0.1647 (5)	0.047 (2)
C(12)	0.7975 (4)	0.1351 (3)	-0.0279 (4)	0.045 (2)
O(13)	0.8133 (3)	0.0722 (2)	0.0053 (3)	0.055 (2)
O(14)	0.7074 (4)	0.1520 (3)	-0.1085 (4)	0.070 (2)
C(15)	1.3967 (4)	0.0743 (3)	0.2604 (4)	0.041 (1)
C(16)	1.4578 (5)	0.1285 (3)	0.2076 (5)	0.053 (2)
C(17)	1.5935 (5)	0.1421 (3)	0.2348 (6)	0.061 (2)
C(18)	1.6688 (5)	0.1005 (4)	0.3192 (6)	0.068 (2)
C(19)	1.6118 (5)	0.0458 (4)	0.3710 (6)	0.066 (2)
C(20)	1.4764 (5)	0.0323 (3)	0.3399 (6)	0.057 (2)
C(21)	1.0471 (4)	-0.0632 (3)	0.3433 (4)	0.039 (1)
C(22)	1.1274 (5)	-0.1214 (3)	0.3550 (5)	0.053 (2)
C(23)	1.0922 (6)	-0.1748 (3)	0.4280 (6)	0.068 (2)
C(24)	0.9838 (6)	-0.1693 (3)	0.4900 (6)	0.067 (2)
C(25)	0.9070 (6)	-0.1114 (3)	0.4782 (5)	0.062 (2)
C(26)	0.9373 (4)	-0.0579 (3)	0.4036 (4)	0.045 (1)
N(27)	0.8198 (4)	-0.0520 (3)	0.1235 (4)	0.048 (1)
C(28)	0.8611 (6)	-0.1161 (3)	0.1253 (4)	0.055 (2)
C(29)	0.7758 (8)	-0.1724 (4)	0.1255 (5)	0.077 (2)
C(30)	0.6424 (8)	-0.1596 (4)	0.1226 (6)	0.083 (2)
C(31)	0.5984 (6)	-0.0929 (4)	0.1169 (6)	0.076 (2)
C(32)	0.6682 (5)	-0.0399 (3)	0.1178 (5)	0.060 (2)

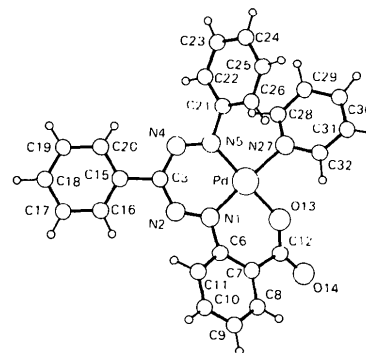


Fig. 1. Projection of the molecule onto the plane of the formazan nucleus.

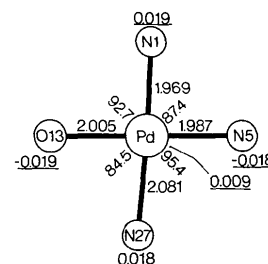


Fig. 2. Coordination of Pd. The underlined numbers are the distances from the best plane through the four coordinating atoms. E.s.d.'s: bonds 0.004 Å, angles 0.2°.

Table 2. Comparison of bond distances (Å) and angles (°) involving the formazan nucleus for various formazan complexes

	PDFORM	NIFORM1	NIFORM3	CUFORM	TTFPd
N(1)–N(2)	1.288 (4)	1.281 (9)	1.302 (4)	1.294 (7)	1.310 (7)
N(2)–C(3)	1.340 (7)	1.347 (8)	1.348 (5)	1.348 (7)	1.351 (8)
C(3)–N(4)	1.359 (7)	1.340 (9)	1.337 (3)	1.338 (7)	1.334 (8)
N(4)–N(5)	1.290 (6)	1.312 (9)	1.318 (4)	1.318 (6)	1.304 (7)
N(1)–C(6)	1.436 (7)	1.413 (8)	1.413 (5)	1.394 (7)	1.409 (7)
C(3)–C(15)	1.472 (6)	1.481 (11)	1.486 (5)	1.486 (7)	1.485 (9)
N(5)–C(21)	1.447 (7)	1.475 (9)	1.454 (5)	1.439 (7)	1.420 (8)
N(1)–N(2)–C(3)	123.9 (4)	119.8 (6)	119.1 (2)	119.0 (5)	121.2 (5)
N(2)–C(3)–N(4)	127.3 (4)	127.8 (7)	128.5 (3)	130.1 (5)	124.1 (6)
C(3)–N(4)–N(5)	121.5 (4)	121.3 (6)	121.0 (3)	123.0 (5)	120.9 (5)

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Structure of the Isothiocyanate Salt of *trans*-Aqua(isothiocyanato)(1,4,8,12-tetraazacyclotetradecane)chromium(III), [Cr(NCS)(H₂O)(C₁₁H₂₆N₄)](NCS)₂

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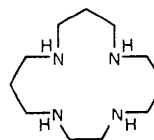
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Abstract. $M_r = 458.6$, orthorhombic, $Pna2_1$, $a = 13.797$ (2), $b = 11.138$ (2), $c = 13.700$ (3) Å, $V = 2105.3$ Å³, $Z = 4$, $D_x = 1.447$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.83$ mm⁻¹, $F(000) = 964$, $T = 291$ K, $R = 0.054$ for 1853 observed reflections. The Cr^{III} atom is coordinated in an equatorial belt by the [15]aneN₄ macrocyclic ligand, and by H₂O and isothiocyanate ligands in mutually *trans* positions. All four N–H bonds are directed to one side of the macrocyclic ligand, away from the H₂O and towards the coordinated NCS⁻. The two uncoordinated NCS⁻ anions are hydrogen bonded to the H₂O ligand.

Introduction. The saturated macrocyclic ligand [15]aneN₄ (1) is one of a series of saturated tetraaza macrocyclic ligands of various ring sizes, complexes of which with various metal ions have been studied structurally. It is found that *cis* isomers are formed by [12]aneN₄ with Co^{III} or Cr^{III}, and by [13]aneN₄ with Cr^{III}, whereas *trans* isomers are formed by [15]aneN₄ or [16]aneN₄ with both metals: for the complexes of [13]aneN₄ and [14]aneN₄ with Co^{III} and of [14]aneN₄

with Cr^{III}, both *cis* and *trans* isomers have been prepared (Collmann & Schneider, 1966; Poon & Tobe, 1967, 1968; Hung, Martin, Jackels, Tait & Busch, 1977; Hung & Busch, 1977; Swisher, Brown, Smierciak & Blinn, 1981). There is evidence of configurational isomerism (different relative orientations of the N–H groups) in [15]aneN₄ complexes of Co^{III} (Hung, Martin, Jackels, Tait & Busch, 1977). We have determined the structure of a [15]aneN₄ complex of Cr^{III} in order to establish the configuration of the macrocyclic ligand in connection with previous kinetic and equilibrium studies in solution (Adzamli, Hender-son, Ong, Sykes, Cammack & Rao, 1982; Richens, Adzamli, Leupin & Sykes, 1984).



[15]aneN₄

(1)