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Crystal structures of bis(L(−)prolinato-*N*)(*trans-R,R*-1,2-diaminocyclohexane)platinum(II) and bis(L(−)prolinato-*N*)-(*cis*-1,2-diaminocyclohexane)platinum(II) complexes

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Abstract

The molecular structures of the compounds bis(L(−)prolinato-*N*)(*trans-R,R*-1,2-diaminocyclohexane)platinum(II) and bis(L(−)prolinato-*N*)(*cis*-1,2-diaminocyclohexane)platinum(II) have been established by single crystal X-ray diffraction. The average plane of the cyclohexane ring of the *cis*-DACH is nearly perpendicular to the PtN_4 plane, while the ring of the *trans-R,R*-DACH is nearly coplanar with PtN_4. Two prolinate ligands are bound to the platinum through amino nitrogen atoms. Crystallographic details: bis(L(−)prolinato-*N*)(*trans-R,R*-1,2-diaminocyclohexane)platinum(II): space group $P2_12_12_1$ (orthorhombic), $a=10.301(2)$, $b=12.364(2)$, $c=17.920(4)$ Å, $Z=4$, $R=0.019$; bis(L(−)prolinato-*N*)(*cis*-1,2-diaminocyclohexane)platinum(II): space group $P2_12_12_1$ (orthorhombic), $a=11.496(5)$, $b=12.918(6)$, $c=16.527(9)$ Å, $Z=4$, $R=0.040$.

Introduction

Platinum(II) complexes with amino acids are well known [1]. However, in most of these complexes, amino acid ligands are bound to the platinum center in a unidentate fashion through the amino nitrogen or in a bidentate fashion through the amino nitrogen and the carboxylate group. Platinum(II) complexes containing amino acid ligands that are bound in a unidentate fashion through the carboxylate oxygen are rare. Compounds with such unidentate bindings have been reported for *cis*-$[Pt(OCO(CH_2)_nNH_3)(OH_2)(NH_3)_2]^{2+}$ and *cis*-$[Pt(OCO(CH_2)_nNH_3)_2(NH_3)_2]^{2+}$ ($n=1$, 2 or 3) [2]. The synthesis of *cis*- and *trans*-$[Pt(OCOCH(NH_3)CH_2NH_3)_2Cl_2]^{2+}$ has also been reported [3]. In both cases, the formation of the oxygen-bound species requires that the reactions are carried out in acidic solution, where the amino group is protonated.

We have investigated a series of (*trans-R,R*-1,2-diaminocyclohexane)platinum(II) and (*cis*-1,2-diaminocyclohexane)platinum(II) complexes containing amino acid ligands as potential antitumor agents and reported the syntheses and spectroscopic characterizations of a series of $[Pt(aa)_2$(*trans-R,R*-DACH)] complexes, where DACH is 1,2-diaminocyclohexane and aa is an amino acid [4]. For complexes with ligands of the type $RR'NCH(R'')COO^-$, the coordination geometry is a function of the substitution at the amino nitrogen. When the amino nitrogen atom is unsubstituted ($R=R'=H$), both amino acid ligands bind to the platinum center through the amino nitrogen forming complexes of the type $[Pt(aa\text{-}N)_2(DACH)]$. But when R or R′ is not H, complexes of the type $[Pt(aa\text{-}N,O)(DACH)]^+[aa]^-$ are also observed.

In this paper, we describe the X-ray crystal structure of two of the $Pt(aa\text{-}N)_2(DACH)$ compounds, bis(L(−)prolinato-*N*)(*trans-R,R*-1,2-diaminocyclohexane)platinum(II) ($Pt(pro\text{-}N)_2$(*trans-R,R*-DACH)) and bis(L(−)prolinato-*N*)(*cis*-1,2-diaminocyclohexane)platinum(II) ($Pt(pro\text{-}N)_2$(*cis*-DACH)).

Experimental

Preparation

$Pt(pro\text{-}N)_2$(*trans-R,R*-DACH) and $Pt(pro\text{-}N)_2$(*cis*-DACH) complexes were prepared by a previously published method [4]. Each compound was dissolved in methanol and left at room temperature to recrystallize. Colorless crystals were formed.

Crystallographic measurements and structure solution

Pt(pro-N)$_2$(trans-R,R-DACH)

A large and clear colorless prismatic column, approximately 0.75 × 0.28 × 0.22 mm, was carved away from

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a very long columnar crystal and mounted on a glass fiber in a random orientation on a Nicolet R3m/V automatic diffractometer. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be *mmm*, and from the systematic absences noted, the space group was shown unambiguously to be $P2_12_12_1$. Intensities were measured using the ω scan technique, with the scan rate depending on the count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data points collected; these showed decay of only 5% over the course of the experiment. In reducing the data, Lorentz and polarization corrcctions were applied, as well as an empirical absorption correction based on ψ scans of ten reflections having χ values between 70 and 90°, max./min. transmission = 0.050/0.021.

The structure was solved by use of the SHELXTL Patterson interpretation program, which revealed the position of the Pt atom. The remaining non-hydrogen atoms were located in subsequent Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions. Only H9 and H15 in the proline rings were allowed to refine independently, the rest being constrained to riding motion. At this point, three solvent molecules were located and were determined to be one methanol and two water molecules. All solvent hydrogens were located in Fourier maps and allowed to refine independently, with a single non-variable isotropic temperature factor for all of them.

Since the compound crystallizes in a non-centrosymmetric, enantiomorphic space group, we attempted to determine empirically the correct absolute configuration. The *R* values for the refinement of the inverted configuration were significantly greater ($R = 0.037/R_w = 0.046$), and when the Bijvöet test [5] was performed using 21 reflections that showed large differences between F_c values for the two separate configurations, all of them indicated the assumed configuration to be the correct one. The DACH moiety is thus *R,R* as shown in the accompanying drawing, which is consistent with the known starting material.

After all shift/e.s.d. ratios were less than 0.5, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed no peaks greater than 0.50 e/A^3.

Pt(pro-N)$_2$(cis-DACH)

A large and clear colorless prism having approximate dimensions 0.70 × 0.45 × 0.35 mm was carved away from a much larger block and then mounted on a glass fiber in a random orientation on a Nicolet R3m/V automatic diffractometer. The data collection were carried out as described for Pt(pro-*N*)$_2$(*trans-R,R*-DACH). The observed linear decay was 10% in this case, max./min. transmission = 0.047/0.025.

A Patterson analysis of the data gave the position of the Pt atom. Subsequent difference Fourier synthesis

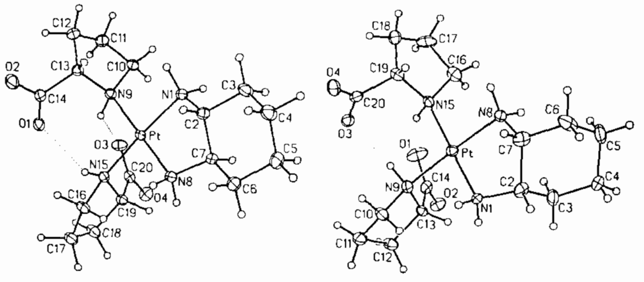
TABLE 1. Data collection and processing parameters

	R,R-DACH	*cis*-DACH
Molecular formula	$C_{16}H_{30}N_4O_4Pt \cdot CH_3OH \cdot 2H_2O$	$C_{16}H_{30}N_4O_4Pt \cdot 6H_2O$
Formula weight	605.68	645.71
Space group	$P2_12_12_1$ (orthorhombic)	$P2_12_12_1$
Cell constants		
a (Å)	10.301(2)	11.496(5)
b (Å)	12.364(2)	12.918(6)
c (Å)	17.920(4)	16.527(9)
V (Å^3)	2282	2454
Formula units per cell, Z	4	4
Density, ρ (g cm^{-3})	1.76	1.75
Absorption coefficient, μ (cm^{-1})	62.5	58.3
Radiation (Mo Kα), (Å)	0.71073	0.71073
Collection range (°)	$4 \leqslant 2\theta \leqslant 58$	$4 \leqslant 2\theta \leqslant 50$
Scan width, $\Delta\omega$ (°)	$1.20 + (K\alpha_2 - K\alpha_1)$	$1.40 + (K\alpha_2 - K\alpha_1)$
Scan speed range (° min^{-1})	2.5–15.0	2.0–15.0
Total data collected	3403	2462
Independent data, $I > 3\sigma(I)$	3162	1981
Total variables	286	280
R	0.019	0.040
R_w	0.022	0.038
Weights, w	$\sigma(F)^{-2}$	$\sigma(F)^{-2}$

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$)

	x	y	z	U_{eq}
R,R-DACH				
Pt	8243(1)	1844(1)	860(1)	31(1)
O(1)	9235(4)	4607(4)	1328(3)	52(2)
O(2)	11223(4)	4617(5)	860(3)	62(2)
O(3)	5908(4)	3769(5)	1028(2)	55(2)
O(4)	4324(4)	3117(5)	1727(3)	59(2)
O(22)	2873(6)	1678(6)	2469(3)	84(3)
O(23)	9299(6)	5402(5)	2745(3)	59(2)
O(24)	12826(7)	4955(5)	2127(4)	65(2)
N(1)	8601(5)	878(4)	−52(3)	36(2)
N(8)	8333(5)	390(4)	1417(2)	37(1)
N(9)	8270(5)	3293(4)	278(2)	35(1)
N(15)	7815(5)	2709(4)	1807(3)	35(1)
C(2)	9061(6)	−201(5)	212(3)	39(2)
C(3)	9001(8)	−1082(6)	−378(3)	56(3)
C(4)	9486(9)	−2151(6)	−57(4)	66(3)
C(5)	8672(9)	−2469(5)	604(4)	63(3)
C(6)	8678(7)	−1588(5)	1206(3)	49(2)
C(7)	8231(6)	−515(4)	876(3)	36(1)
C(10)	7579(6)	3367(5)	−462(3)	44(2)
C(11)	7987(7)	4483(6)	−730(3)	54(2)
C(12)	9434(7)	4549(6)	−524(4)	54(2)
C(13)	9603(6)	3780(5)	152(3)	37(2)
C(14)	10065(5)	4371(5)	852(4)	41(2)
C(16)	8614(6)	2491(6)	2506(3)	45(2)
C(17)	7833(6)	2940(7)	3148(3)	52(2)
C(18)	6491(6)	3136(8)	2862(3)	60(2)
C(19)	6446(5)	2649(5)	2073(3)	39(2)
C(20)	5499(5)	3239(6)	1553(3)	40(2)
C(21)	3604(9)	1225(8)	3058(5)	81(4)
cis-DACH				
Pt	4825(1)	8622(1)	5643(1)	35(1)
O(1)	3489(10)	6708(15)	6860(10)	78(8)
O(2)	1898(9)	6208(12)	6264(7)	61(5)
O(3)	6439(10)	6542(13)	6735(8)	48(5)
O(4)	8059(10)	7380(10)	6507(8)	59(5)
N(1)	4544(10)	8957(9)	4451(7)	34(4)
N(8)	4885(13)	10206(9)	5766(8)	53(5)
N(9)	4687(12)	7036(9)	5479(8)	44(5)
N(15)	5229(12)	8364(9)	6842(7)	38(4)
C(2)	4236(13)	10047(12)	4311(12)	48(6)
C(3)	2973(15)	10257(14)	4459(16)	61(8)
C(4)	2714(17)	11413(16)	4394(13)	84(8)
C(5)	3361(19)	12039(15)	5057(16)	77(10)
C(6)	4720(25)	11821(15)	4904(11)	69(9)
C(7)	5020(23)	10695(14)	4927(9)	56(8)
C(10)	5353(18)	6586(13)	4783(10)	54(7)
C(11)	4904(21)	5489(13)	4740(11)	60(7)
C(12)	3629(15)	5582(15)	4950(11)	52(7)
C(13)	3481(14)	6621(12)	5419(8)	35(6)
C(14)	2907(15)	6522(16)	6265(10)	42(6)
C(16)	4732(16)	9009(13)	7472(10)	56(7)
C(17)	5498(19)	8732(21)	8165(11)	106(11)
C(18)	6652(14)	8464(18)	7888(11)	57(8)
C(19)	6538(13)	8332(13)	7018(10)	42(6)
C(20)	7058(15)	7325(16)	6721(11)	41(7)
O(21)	2304(11)	9441(10)	1854(8)	55(5)
O(22)	4507(10)	6515(11)	2592(7)	70(5)
O(23)	8219(11)	8900(10)	1621(8)	63(6)
O(24)	6817(11)	6389(14)	2945(10)	91(6)
O(25)	4319(11)	8354(11)	1665(8)	85(6)
O(26)	6084(12)	9460(11)	2322(8)	77(6)

revealed the remaining non-hydrogen atoms. Six independent water molecules of solvation were also found, but all attempts to locate their hydrogen atoms failed. Even when rigid body models were refined, the hydrogens went to unreasonable locations with respect to neighboring molecules. Therefore it was decided to exclude the water hydrogens entirely rather than allow



(a) (b)

Fig. 1. View of the molecules, with atom-labeling schemes. The thermal ellipsoids are 20% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter. Intramolecular hydrogen bonds are indicated by dotted lines. (a) Pt(pro-*N*)$_2$(*trans*-*R*,*R*-DACH) and (b) Pt(pro-*N*)$_2$(*cis*-DACH).

TABLE 3. Bond lengths (Å)

R,R-DACH			
Pt–N(1)	2.058(5)	Pt–N(8)	2.058(5)
Pt–N(9)	2.074(5)	Pt–N(15)	2.054(5)
O(1)–C(14)	1.242(7)	O(2)–C(14)	1.231(6)
O(3)–C(20)	1.221(7)	O(4)–C(20)	1.259(7)
O(22)–C(21)	1.412(10)	O(22)–H(22)	0.895(82)
O(23)–H(23A)	0.682(83)	O(23)–H(23B)	0.850(80)
O(24)–H(24A)	0.565(90)	O(24)–H(24B)	1.079(79)
N(1)–C(2)	1.493(7)	N(8)–C(7)	1.483(7)
N(9)–C(10)	1.507(7)	N(9)–C(13)	1.517(8)
N(9)–H(9)	1.114(68)	N(15)–C(16)	1.523(8)
N(15)–C(19)	1.491(8)	N(15)–H(15)	0.738(83)
C(2)–C(3)	1.520(8)	C(2)–C(7)	1.516(8)
C(3)–C(4)	1.525(9)	C(4)–C(5)	1.504(10)
C(5)–C(6)	1.533(9)	C(6)–C(7)	1.523(8)
C(10)–C(11)	1.521(9)	C(11)–C(12)	1.538(9)
C(12)–C(13)	1.550(9)	C(13)–C(14)	1.528(8)
C(16)–C(17)	1.510(8)	C(17)–C(18)	1.495(9)
C(18)–C(19)	1.537(8)	C(19)–C(20)	1.535(8)
cis-DACH			
Pt–N(1)	2.041(6)	Pt–N(8)	2.057(5)
Pt–N(9)	2.073(6)	Pt–N(15)	2.062(5)
O(1)–C(14)	1.213(11)	O(2)–C(14)	1.229(10)
O(3)–C(20)	1.237(12)	O(4)–C(20)	1.205(10)
N(1)–C(2)	1.470(10)	N(8)–C(7)	1.531(10)
N(9)–C(10)	1.499(11)	N(9)–C(13)	1.490(10)
N(15)–C(16)	1.451(10)	N(15)–C(19)	1.534(10)
C(2)–C(3)	1.497(12)	C(2)–C(7)	1.598(13)
C(3)–C(4)	1.527(14)	C(4)–C(5)	1.552(15)
C(5)–C(6)	1.608(17)	C(6)–C(7)	1.495(13)
C(10)–C(11)	1.510(12)	C(11)–C(12)	1.511(14)
C(12)–C(13)	1.560(12)	C(13)–C(14)	1.551(11)
C(16)–C(17)	1.488(13)	C(17)–C(18)	1.446(14)
C(18)–C(19)	1.454(12)	C(19)–C(20)	1.514(13)

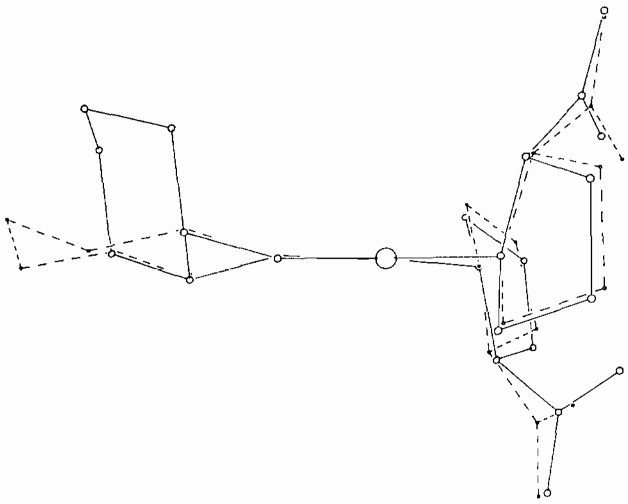


Fig. 2. Least-squares fit between the 4N planes of the *cis* (large circles) and *trans* (small circles) DACH molecules.

them to refine to possibly false and misleading locations. The Rogers test [6] was performed and indicated conclusively that the correct absolute configuration is the one reported herein. After all shift/e.s.d. ratios were less than 0.2, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.8 e/Å^3. Final bond distances and angles were based on the atomic coordinates given in Table 2.

Results and discussion

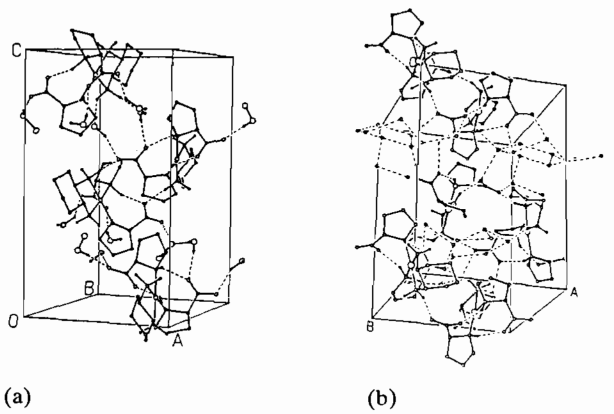
The molecular structures of Pt(pro-*N*)$_2$(*trans-R,R*-DACH) and Pt(pro-*N*)$_2$(*cis*-DACH) have been determined, and their absolute configurations have been established by X-ray crystallographic techniques. Figure 1 shows both molecules along with their atom labeling. Two adjacent corners of the platinum plane are occupied by the nitrogens of the bidentate DACH ligand, and the remaining *cis* corners are bound by nitrogens of two monodentate prolines. The coordination about the platinum atom is essentially square planar, with a slight compression of the N1–Pt–N8 angles caused by the limited bite width of DACH.

These crystal structures verify the previous spectral assignment of two prolinate ligands bound to platinum through the amino nitrogen atoms [4]. The four Pt–N distances (mean 2.061 and 2.058 Å for the *trans-R,R*-DACH and *cis*-DACH compounds, respectively (Table 3)) are similar to those found for Pt(oxalato)(1*R*,2*R*-cyclohexanediamine) (2.05 Å) [7], *trans-d,l*-1,2-diaminocyclohexane(*N*-methyliminodiacetato)platinum(II) (2.038 Å) [8] and bis(acetato)(*trans*-1,2-diaminocyclohexane)platinum(II) (2.00 Å) [9]. *trans-R,R*- and *cis*-DACH bidentate ligands impose N1–Pt–N8 angles of 82.5 and 83.7° (Table 4), respectively, with the platinum atom, which is typical of five-membered rings with similar donor atoms. However, in both cases, the N15–Pt–N9 angle formed with two prolinate ligands is somewhat smaller than 90°, possibly due to the formation of two hydrogen bonds between the ligands.

TABLE 4. Bond angles (°)

R,R-DACH			
N(8)–Pt–N(1)	82.5(2)	N(9)–Pt–N(1)	95.7(2)
N(9)–Pt–N(8)	176.5(2)	N(15)–Pt–N(1)	175.6(2)
N(15)–Pt–N(8)	93.7(2)	N(15)–Pt–N(9)	88.2(2)
H(22)–O(22)–C(21)	112.5(57)	H(23B)–O(23)–H(23A)	108.5(91)
H(24B)–O(24)–H(24A)	115.7(122)	C(2)–N(1)–Pt	108.9(3)
C(7)–N(8)–Pt	109.8(3)	C(10)–N(9)–Pt	119.3(4)
C(13)–N(9)–Pt	115.5(4)	C(13)–N(9)–C(10)	105.8(4)
H(9)–N(9)–Pt	94.6(37)	H(9)–N(9)–C(10)	105.3(35)
H(9)–N(9)–C(13)	116.1(36)	C(16)–N(15)–Pt	118.1(4)
C(19)–N(15)–Pt	116.2(4)	C(19)–N(15)–C(16)	103.9(5)
H(15)–N(15)–Pt	123.0(67)	H(15)–N(15)–C(16)	88.8(65)
H(15)–N(15)–C(19)	102.2(69)	C(3)–C(2)–N(1)	114.0(5)
C(7)–C(2)–N(1)	107.4(5)	C(7)–C(2)–C(3)	109.9(5)
C(4)–C(3)–C(2)	110.2(5)	C(5)–C(4)–C(3)	110.0(7)
C(6)–C(5)–C(4)	111.5(6)	C(7)–C(6)–C(5)	110.2(5)
C(2)–C(7)–N(8)	106.2(5)	C(6)–C(7)–N(8)	112.5(4)
C(6)–C(7)–C(2)	110.9(5)	C(11)–C(10)–N(9)	101.7(5)
C(12)–C(11)–C(10)	103.9(5)	C(13)–C(12)–C(11)	105.3(5)
C(12)–C(13)–N(9)	104.9(5)	C(14)–C(13)–N(9)	110.5(5)
C(14)–C(13)–C(12)	112.6(5)	O(2)–C(14)–O(1)	127.0(6)
C(13)–C(14)–O(1)	117.5(5)	C(13)–C(14)–O(2)	115.4(6)
C(17)–C(16)–N(15)	105.9(5)	C(18)–C(17)–C(16)	106.9(5)
C(19)–C(18)–C(17)	106.3(6)	C(18)–C(19)–N(15)	104.3(5)
C(20)–C(19)–N(15)	112.5(5)	C(20)–C(19)–C(18)	113.1(6)
O(4)–C(20)–O(3)	126.0(6)	C(19)–C(20)–O(3)	120.3(5)
C(19)–C(20)–O(4)	113.8(6)		
cis-DACH			
N(1)–Pt–N(8)	83.7(2)	N(1)–Pt–N(9)	94.1(2)
N(8)–Pt–N(9)	176.9(3)	N(1)–Pt–N(15)	175.2(2)
N(8)–Pt–N(15)	93.4(2)	N(9)–Pt–N(15)	89.0(2)
Pt–N(1)–C(2)	113.2(5)	Pt–N(8)–C(7)	108.9(5)
Pt–N(9)–C(10)	116.4(5)	Pt–N(9)–C(13)	115.8(4)
C(10)–N(9)–C(13)	106.5(6)	Pt–N(15)–C(16)	120.6(5)
Pt–N(15)–C(19)	114.1(4)	C(16)–N(15)–C(19)	105.3(6)
N(1)–C(2)–C(3)	112.4(6)	N(1)–C(2)–C(7)	105.4(6)
C(3)–C(2)–C(7)	110.3(8)	C(2)–C(3)–C(4)	110.8(7)
C(3)–C(4)–C(5)	111.4(8)	C(4)–C(5)–C(6)	105.3(8)
C(5)–C(6)–C(7)	113.0(9)	N(8)–C(7)–C(2)	107.6(7)
N(8)–C(7)–C(6)	113.7(7)	C(2)–C(7)–C(6)	111.3(8)
N(9)–C(10)–C(11)	103.0(7)	C(10)–C(11)–C(12)	104.2(7)
C(11)–C(12)–C(13)	106.7(7)	N(9)–C(13)–C(12)	104.0(6)
N(9)–C(13)–C(14)	111.5(6)	C(12)–C(13)–C(14)	115.0(7)
O(1)–C(14)–O(2)	125.9(8)	O(1)–C(14)–C(13)	118.6(8)
O(2)–C(14)–C(13)	115.4(7)	N(15)–C(16)–C(17)	100.5(7)
C(16)–C(17)–C(18)	110.9(7)	C(17)–C(18)–C(19)	105.0(7)
N(15)–C(19)–C(18)	105.8(6)	N(15)–C(19)–C(20)	110.4(6)
C(18)–C(19)–C(20)	112.7(7)	O(3)–C(20)–O(4)	127.1(9)
O(3)–C(20)–C(19)	118.0(7)	O(4)–C(20)–C(19)	114.9(8)

The configuration of the DACH molecules described in this work agrees with previously reported configurations [7–9]. The chelate rings obtained from the coordination of *trans-R,R*- and *cis*-DACH are puckered



(a) (b)

Fig. 3. View of the molecular packing in the unit cell, with hydrogens attached to carbon omitted for clarity. Atoms that are probably involved in hydrogen bonding are indicated by dashed lines. (a) Pt(pro-*N*)$_2$(*trans-R,R*-DACH) and (b) Pt(pro-*N*)$_2$(*cis*-DACH).

TABLE 5. Hydrogen bonding parameters

A–H···B	A–H	A···B	H···B	<H
R,R-DACH				
N(1),H(1A),O(3)	1.05	2.98	2.00	155
N(1),H(1B),O(2)	1.05	2.91	1.87	171
N(8),H(8A),O(24)	1.05	2.92	2.02	142
N(8),H(8B),O(23)	1.05	2.87	1.82	173
N(9),H(9),O(3)	1.11	2.84	1.88	142
N(15),H(15),O(1)	0.74	2.90	2.29	140
O(22),H(22),O(4)	0.90	2.68	1.80	165
O(23),H(23A),O(1)	0.68	2.72	2.06	165
O(23),H(23B),O(22)	0.85	2.76	1.94	165
O(24),H(24A),O(4)	0.57	2.84	2.31	156
O(24),H(24B),O(2)	1.08	2.84	1.90	144
cis-DACH				
N(1),H(1A),O(4)	0.96	2.90	1.99	157
N(1),H(1B),O(2)	0.96	2.96	2.03	164
N(8),H(8A),O(23)	0.96	2.84	1.91	165
N(8),H(8B),O(21)	0.96	3.13	2.21	160
N(9),H(9),O(3)	0.96	2.96	2.07	154
N(15),H(15),O(1)	0.96	2.93	2.03	156
O(21),,O(3)		2.84		
O(21),,O(24)		2.73		
O(21),,O(25)		2.73		
O(22),,O(4)		2.65		
O(22),,O(24)		2.72		
O(22),,O(25)		2.84		
O(22),,O(26)		2.74		
O(23),,O(1)		2.65		
O(23),,O(26)		2.81		
O(24),,O(1)		3.14		
O(25),,O(26)		2.71		
O(26),,O(2)		2.66		

with a 'λ' conformation, as evidenced by the negative N1–C2–C7–N8 torsion angles (−54.8 and −49.7°, respectively).

Both Pt(pro-*N*)$_2$(*trans-R,R*-DACH) and Pt(pro-*N*)$_2$(*cis*-DACH) molecules are zwitterions. The central 2+ positive charge on Pt is balanced by negative charges on both of the unbound carboxylate groups. Furthermore, the carboxylate groups on the prolines are completely delocalized, since all C–O bond distances are equivalent (Table 3).

Figure 2 shows the least-squares fit between the 4N planes of the *cis*- and *trans-R,R*-DACH molecules. The cyclohexane ring in the *cis*-DACH complex is nearly perpendicular to the chelate ring PtN_4, whereas that of the *trans-R,R*-DACH complex is more nearly coplanar. Specifically, for *cis*-DACH, the dihedral angle between the PtN_4 coordination plane and the mean plane through the cyclohexane ring is 66.2°. This value is in agreement with that of ~67° for the angle between the PtO_2N_2 plane and the cyclohexane ring mean plane [10]. In *trans-R,R*-DACH, this same dihedral angle is 8.3°, comparable with values reported in structurally related complexes (13° [7], 11° [7] and 19° [9]).

Figure 3 gives the molecular packing in the unit cells in which the strong hydrogen bonding networks can be seen. This extensive system of intra- and intermolecular hydrogen bonds involves all oxygen and nitrogen atoms (Table 5).

Supplementary material

Observed and calculated structure factors as well as anisotropic thermal parameters and hydrogen atomic coordinates can be obtained from the authors on request.

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References

1 F. R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science, London, 1973, pp. 205–209.

2 T. G. Appleton, J. R. Hall and S. F. Ralph, *Aust. J. Chem., 39* (1986) 1347.

3 J. Altman and M. Wilchek, *Inorg. Chim. Acta, 101* (1985) 171.

4 A. R. Khokhar and G. J. Lumetta, *J. Coord. Chem., 26* (1992) 251.

5 J. M. Bijvöet, A. F. Peerdeman and A. J. Van Bommel, *Nature (London), 168* (1951) 271.

6 D. Rogers, *Acta Crystallogr., Sect. A, 37* (1981) 734.

7 M. A. Bruck, R. Bau, M. Noji, K. Inagaki and Y. Kidani, *Inorg. Chim. Acta, 92* (1984) 279.

8 A. R. Khokhar, Q. Xu, S. Al-Baker and J. L. Bear, *Inorg. Chim. Acta, 194* (1992) 243.

9 F. D. Rochon, R. Melanson, J.-P. Macquet, F. Belanger-Gariepy and A. L. Beauchamp, *Inorg. Chim. Acta, 108* (1985) 17.

10 C. J. L. Lock and P. Pilon, *Acta Crystallogr., Sect. B, 37* (1981) 45.