Crystal structure of dichloro{[anilino(phenylimino)methyl]-(propanimidoyl)azanide}-[η^2-(*N*,*N'*-diphenylguanidinato)]platinum(IV) — deuterochloroform (1:1), $PtCl_2(C_{13}H_{12}N_3)(C_{16}H_{17}N_4) \cdot CDCl_3$

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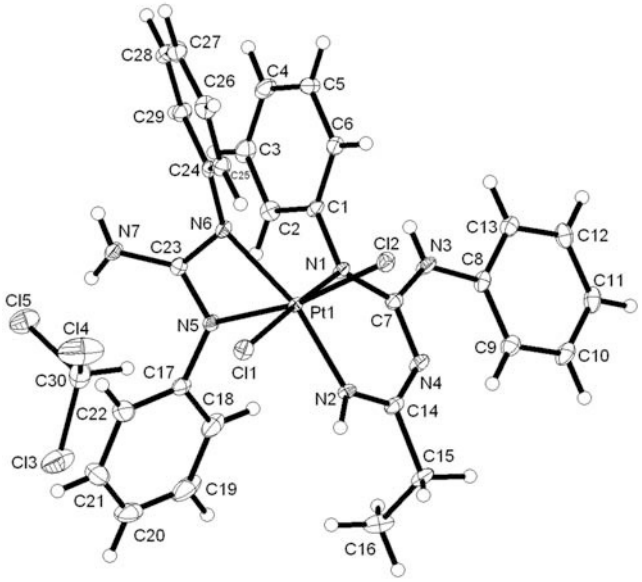

Abstract

$C_{30}H_{29}Cl_5DN_7Pt$, monoclinic, $P12_1/n1$ (no. 14), a = 12.555(1) Å, b = 14.136(1) Å, c = 18.151(2) Å, β = 100.804(8)°, V = 3164.3 Å^3, Z = 4, $R_{gt(F)}$ = 0.019, $wR_{ref}(F^2)$ = 0.037, T = 100 K.

Source of material

Diphenylguanidine (129.7 mg, 0.61 mmol) was added to a suspension of the *trans*-$[PtCl_4(EtCN)_2]$ complex (0.15 mmol) in CH_2Cl_2 (2 mL) at 293 - 298 K. The reaction mixture was stirred for 18 h. The resulting orange-red solution was evaporated until dryness. The red oily residue was dissolved in $CHCl_3$ (0.75 mL), and the complex was isolated by silica gel.

Experimental details

The NH_2O and NH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atoms, with U_{iso} = 1.2 - 1.5 U_{eq}(parent atom). Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with d(C—H) = 0.95 - 1.00 Å, and U_{iso} = 1.2 - 1.5 U_{eq}(parent atom). The highest peak of the residual density map is located 0.78 Å from atom Cl4 and the deepest hole is located 0.79 Å from atom Cl4.

Discussion

The coordination polyhedron of the title complex is a distorted octahedron. The Pt^{Iv} centre is coordinated by two N atoms of the chelating triazapentadienato ligand, two N atoms of the chelating guanidinato species, and two Cl atoms. The 1,3,5-triazapentadienato ligand forms an almost planar Pt–N–C–N–C–N platinacycle (maximum deviation: 0.070(2) Å) while the *N*,*N'*-diphenylguanidinato ligand is part of a non-planar Pt–N–C–N platinacycle. The angle between the diphenylguanidine plane N–N–N–C (including the N of the NH_2 group) and the plane of the six-membered 1,3,5-triazapentadienatometallacycle Pt–N–C–N–C–N is 79.91(9)°. The angles of the triazapentadienato and the diphenylguanidine ligands are 89.21(6)° and 63.78(6)°, respectively.

The C—N bonds in the six-membered metallacycle are clearly different. The N2—C14 bond length of 1.303(2) Å resembles C=N double bonds in the monochelate and bischelate (1,3,5-triazapentadienato)Pt^{II} complexes, *viz*., [PtCl{N(H)C(Et)NC-(N(H)Ph)NPh}(EtCN)] (II) (1.313(4) Å) and [Pt{N(H)=C(Et)-NC(N(H)Ph)NPh}$_2$] (III) (1.306(3) Å), respectively [1], and the monochelate (1,3,5-triazapentadienato)Pt^{IV}complex $[PtCl_3\{N(H)C(NHPh)_2\}\{N(H)=C(Et)NC(N(H)Ph)=NPh\}]$ (1.298(4) Å) [2]. The N4—C14 and N4—C7 bond lengths (1.330(3) and 1.334(2) Å, respectively) are close to the N—C bond lengths in Pt^{II} and Pt^{IV} complexes containing the Pt—N(H)=C(Et)NC(N(H)Ph)=NPh moiety [1,2]. The N1—C7 distance (1.333(2) Å) is longer than a typical N=C double bonds in the (1,3,5-triazapentadiene)*M* and/or (1,3,5-triazapentadienato)*M* (*M* = Pt^{II} or Ni^{II}) complexes [1,3,4], due to the influence of the N(H)Ph group. However, this interatomic distance is typical (within 3σ) for this type of 1,3,5-triazapentadiene- and/or 1,3,5-triazapentadienato-containing metallacycles, and is comparable with the lengths of the corresponding C=N double bonds in the monochelated and bischelated (1,3,5-triazapentadienato)Pt^{II} complexes[1] and the monochelated (1,3,5-triazapentadienato)Pt^{IV} complex [2]. The N=C double bond lengths and the N—C single bond lengths in the metallacycle, in contrast to complexes of the types (1,3,5-triazapentadiene)*M* and/or (1,3,5-triazapentadienato)*M* (*M* = Pt^{II}or Ni^{II}) [1,3,4], are indicative of a higher degree of delocalization in the metallacycle. The N3—C7 bond distance (1.370 (2) Å) is similar to the length of the corresponding N—C single bond in Pt^{II} and Pt^{IV} complexes containing the analogous structural fragment, i.e. PtN(H)=C(Et)NC(N(H)Ph)=NPh [1,2]. The N5—C23 and N6—C23 bond lengths (1.352(2) and 1.327(2) Å, respectively)

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within the four-membered chelate ring formed by η^2-diphenylguanidinato ligand are similar (within 3σ) to those found in related CN bonds in the $(NPh)_2C—N(H)_2$ η^2-*N*,*N*′-diphenylguanidinato ligand in the Mo complex [5], and $(NPh)_2C—NHPh$ η^2-*N*,*N*′,*N*″-triphenylguanidinato ligand in the Pt, Pd, Ru and Mo complexes [5-8], as well as to the CN bonds found in the η^2-$(NPh)_2CNEt_2$ ligand in some Ti complexes [6]. Such bond lengths are consistent with the presence of a delocalized NCN ligand backbone. An inspection of the bond length and angle values suggests that there is a small delocalization of the lone pair on the N7 non-coordinated N over the guanidine skeleton.

Table 1. Data collection and handling.

Crystal:	red block, size 0.15 × 0.18 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	48.91 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, φ/ω with κ offset
$2\theta_{max}$:	60°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	65894, 9239
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7787
$N(param)_{refined}$:	389
Programs:	SHELXS-97 [9], SHELXL-97 [10], DIAMOND [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2N)	4*e*	0.8812	0.7914	0.1832	0.019
H(3N)	4*e*	0.8198	0.5896	–0.0849	0.023
H(7N)	4*e*	0.9216	0.3778	0.2443	0.025
H(7M)	4*e*	0.8100	0.3465	0.2275	0.025
H(2)	4*e*	0.9332	0.4589	0.0401	0.018
H(3)	4*e*	0.8882	0.3077	–0.0072	0.022
H(4)	4*e*	0.7101	0.2722	–0.0619	0.024
H(5)	4*e*	0.5748	0.3863	–0.0682	0.021
H(6)	4*e*	0.6187	0.5385	–0.0210	0.017
H(9)	4*e*	0.9761	0.7948	–0.0788	0.020
H(10)	4*e*	1.0268	0.8575	–0.1857	0.022
H(11)	4*e*	0.9651	0.7922	–0.3033	0.022
H(12)	4*e*	0.8513	0.6594	–0.3145	0.020
H(13)	4*e*	0.8004	0.5949	–0.2085	0.018
H(15A)	4*e*	0.9430	0.9171	0.1399	0.022
H(15B)	4*e*	0.9670	0.9124	0.0563	0.022
H(16A)	4*e*	1.0950	0.8175	0.1824	0.036
H(16B)	4*e*	1.1329	0.9103	0.1439	0.036
H(16C)	4*e*	1.1189	0.8123	0.0989	0.036
H(18)	4*e*	1.0669	0.6094	0.1461	0.028
H(19)	4*e*	1.2369	0.6421	0.2179	0.046
H(20)	4*e*	1.2715	0.6115	0.3460	0.052
H(21)	4*e*	1.1360	0.5483	0.4032	0.043
H(22)	4*e*	0.9653	0.5151	0.3320	0.026
H(25)	4*e*	0.5620	0.5586	0.2104	0.017
H(26)	4*e*	0.4011	0.4786	0.2159	0.022
H(27)	4*e*	0.3763	0.3230	0.1725	0.023
H(28)	4*e*	0.5099	0.2498	0.1198	0.023
H(29)	4*e*	0.6699	0.3297	0.1117	0.017
D(30)	4*e*	0.7895	0.5955	0.3872	0.030

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	4*e*	0.780605(5)	0.634505(5)	0.145010(4)	0.00934(3)	0.00653(3)	0.01067(3)	–0.00037(3)	0.00270(2)	–0.00003(3)
Cl(1)	4*e*	0.75538(4)	0.67131(3)	0.26525(3)	0.0201(2)	0.0127(2)	0.0130(2)	0.0006(2)	0.0053(2)	–0.0022(2)
Cl(2)	4*e*	0.62315(4)	0.71648(3)	0.09175(3)	0.0119(2)	0.0129(2)	0.0206(2)	0.0017(2)	0.0021(2)	0.0031(2)
Cl(3)	4*e*	0.91505(5)	0.61333(4)	0.49437(4)	0.0286(3)	0.0211(3)	0.0523(4)	–0.0045(2)	0.0089(3)	–0.0064(3)
Cl(4)	4*e*	0.68396(5)	0.58901(5)	0.47624(5)	0.0264(3)	0.0380(4)	0.0841(6)	0.0035(3)	0.0110(3)	–0.0305(4)
Cl(5)	4*e*	0.81253(5)	0.44279(4)	0.42614(3)	0.0276(3)	0.0198(3)	0.0354(3)	–0.0009(2)	0.0095(2)	–0.0075(2)
N(1)	4*e*	0.8084(1)	0.6055(1)	0.04189(9)	0.0142(7)	0.0080(7)	0.0118(7)	–0.0023(6)	0.0051(6)	–0.0002(6)
N(2)	4*e*	0.8636(1)	0.7536(1)	0.14454(9)	0.0147(8)	0.0083(8)	0.0144(8)	–0.0023(6)	0.0011(6)	–0.0021(6)
N(3)	4*e*	0.8472(1)	0.6424(1)	–0.07295(9)	0.0224(8)	0.0116(8)	0.0141(8)	–0.0075(7)	0.0067(6)	–0.0002(7)
N(4)	4*e*	0.8938(1)	0.7523(1)	0.02037(9)	0.0176(8)	0.0099(8)	0.0166(8)	–0.0035(6)	0.0060(7)	–0.0004(6)
N(5)	4*e*	0.8995(1)	0.5397(1)	0.18580(9)	0.0100(7)	0.0090(8)	0.0162(8)	0.0005(6)	0.0010(6)	0.0013(6)
N(6)	4*e*	0.7305(1)	0.4991(1)	0.16113(9)	0.0110(7)	0.0079(7)	0.0142(8)	0.0004(6)	0.0039(6)	0.0011(6)
N(7)	4*e*	0.8547(1)	0.3887(1)	0.2289(1)	0.0118(7)	0.0103(8)	0.0255(9)	–0.0010(6)	–0.0005(7)	0.0046(7)
C(1)	4*e*	0.7800(2)	0.5129(1)	0.0132(1)	0.0167(9)	0.0095(9)	0.0106(8)	–0.0033(7)	0.0055(7)	0.0004(7)
C(2)	4*e*	0.8604(2)	0.4443(1)	0.0178(1)	0.0155(9)	0.016(1)	0.0148(9)	–0.0002(8)	0.0047(8)	–0.0005(8)
C(3)	4*e*	0.8336(2)	0.3548(1)	–0.0102(1)	0.026(1)	0.012(1)	0.019(1)	0.0038(8)	0.0056(8)	–0.0022(8)
C(4)	4*e*	0.7279(2)	0.3337(2)	–0.0424(1)	0.032(1)	0.0114(9)	0.016(1)	–0.0049(9)	0.0044(9)	–0.0032(8)
C(5)	4*e*	0.6477(2)	0.4015(2)	–0.0464(1)	0.019(1)	0.017(1)	0.0156(9)	–0.0067(8)	–0.0008(8)	0.0000(8)
C(6)	4*e*	0.6735(2)	0.4917(1)	–0.0184(1)	0.0168(9)	0.0118(9)	0.0133(9)	–0.0008(7)	0.0022(7)	0.0013(7)
C(7)	4*e*	0.8493(2)	0.6684(1)	0.0000(1)	0.0103(8)	0.0112(9)	0.0150(9)	0.0000(7)	0.0025(7)	0.0002(7)
C(8)	4*e*	0.8824(2)	0.6884(1)	–0.1329(1)	0.0128(9)	0.0130(9)	0.0157(9)	0.0022(7)	0.0063(7)	0.0035(7)
C(9)	4*e*	0.9504(2)	0.7669(1)	–0.1265(1)	0.0168(9)	0.016(1)	0.018(1)	–0.0022(8)	0.0055(8)	0.0021(8)
C(10)	4*e*	0.9802(2)	0.8040(2)	–0.1903(1)	0.0148(9)	0.016(1)	0.025(1)	–0.0015(8)	0.0084(8)	0.0065(8)
C(11)	4*e*	0.9441(2)	0.7655(2)	–0.2602(1)	0.0154(9)	0.022(1)	0.020(1)	0.0047(8)	0.0093(8)	0.0104(8)
C(12)	4*e*	0.8766(2)	0.6869(2)	–0.2667(1)	0.0162(9)	0.019(1)	0.0150(9)	0.0065(8)	0.0041(8)	0.0032(8)
C(13)	4*e*	0.8463(2)	0.6488(1)	–0.2037(1)	0.0138(9)	0.013(1)	0.0179(9)	0.0010(7)	0.0047(7)	0.0021(7)
C(14)	4*e*	0.9038(2)	0.7882(1)	0.0891(1)	0.0111(8)	0.0087(9)	0.021(1)	–0.0001(7)	0.0037(7)	0.0000(7)
C(15)	4*e*	0.9716(2)	0.8765(1)	0.1037(1)	0.021(1)	0.011(1)	0.023(1)	–0.0067(8)	0.0063(8)	–0.0010(8)
C(16)	4*e*	1.0903(2)	0.8520(2)	0.1351(1)	0.019(1)	0.022(1)	0.032(1)	–0.0075(9)	0.0082(9)	–0.0102(9)
C(17)	4*e*	1.0003(2)	0.5577(1)	0.2322(1)	0.0109(8)	0.0084(9)	0.024(1)	0.0017(7)	0.0014(8)	0.0003(8)
C(18)	4*e*	1.0810(2)	0.5965(2)	0.1984(1)	0.017(1)	0.014(1)	0.041(1)	0.0003(8)	0.0067(9)	0.006(1)
C(19)	4*e*	1.1816(2)	0.6161(2)	0.2410(2)	0.014(1)	0.019(1)	0.080(2)	–0.0039(9)	0.003(1)	0.013(1)
C(20)	4*e*	1.2020(2)	0.5981(2)	0.3169(2)	0.021(1)	0.020(1)	0.076(2)	–0.005(1)	–0.023(1)	0.008(1)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(21)	4*e*	1.1217(2)	0.5604(2)	0.3508(2)	0.037(1)	0.022(1)	0.039(1)	–0.001(1)	–0.019(1)	0.001(1)
C(22)	4*e*	1.0206(2)	0.5405(2)	0.3087(1)	0.021(1)	0.018(1)	0.024(1)	–0.0002(9)	–0.0009(9)	–0.0006(9)
C(23)	4*e*	0.8285(2)	0.4704(1)	0.1943(1)	0.0130(8)	0.0098(9)	0.0112(8)	0.0010(7)	0.0037(7)	–0.0009(7)
C(24)	4*e*	0.6328(2)	0.4509(1)	0.1625(1)	0.0111(8)	0.0109(9)	0.0099(8)	–0.0006(7)	0.0011(7)	0.0033(7)
C(25)	4*e*	0.5519(2)	0.4955(1)	0.1923(1)	0.0160(9)	0.0130(9)	0.0146(9)	0.0008(7)	0.0036(7)	0.0001(7)
C(26)	4*e*	0.4564(2)	0.4480(2)	0.1955(1)	0.0125(9)	0.022(1)	0.022(1)	0.0021(8)	0.0063(8)	0.0038(9)
C(27)	4*e*	0.4412(2)	0.3559(2)	0.1692(1)	0.0122(9)	0.022(1)	0.023(1)	–0.0043(8)	0.0017(8)	0.0076(9)
C(28)	4*e*	0.5206(2)	0.3126(2)	0.1384(1)	0.018(1)	0.012(1)	0.025(1)	–0.0028(8)	–0.0002(8)	0.0020(8)
C(29)	4*e*	0.6161(2)	0.3596(1)	0.1340(1)	0.0154(9)	0.0106(9)	0.0178(9)	0.0011(8)	0.0034(7)	–0.0005(8)
C(30)	4*e*	0.7992(2)	0.5649(2)	0.4377(1)	0.035(1)	0.019(1)	0.022(1)	0.003(1)	0.005(1)	0.0019(9)

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