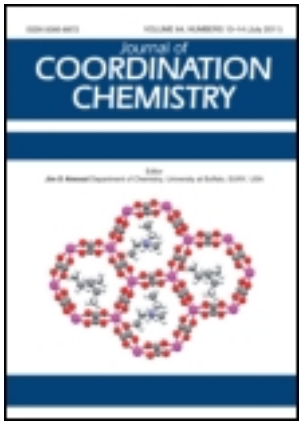

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Platinum(II) complexes containing the 3,3-dimethylglutarimidate ligand

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Platinum(II) complexes containing the 3,3-dimethylglutarimidate ligand

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Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with excess 3,3-dimethylglutarimide (dmgH) and sodium chloride in refluxing methanol gives the mono-imidate complex *cis*-$[PtCl(dmg)(PPh_3)_2]$, which was structurally characterized. The plane of the imidate ligand is approximately perpendicular to the platinum coordination plane which, coupled with restricted rotation about the Pt–N bond, results in inequivalent methyl groups and CH_2 protons of the dmg ligand in the room temperature ^1H NMR spectrum. These observations were corroborated by a theoretical study using density functional theory methods. The analogous bromide complex *cis*-$[PtBr(dmg)(PPh_3)_2]$ can be prepared by replacing NaCl with NaBr in the reaction mixture.

Keywords: Platinum complexes; Imidate complexes; Crystal structure; Theoretical calculations

1. Introduction

While platinum(II) is typically classified as a soft metal center, with a strong affinity for sulfur and phosphorus donors [1], a considerable number of platinum complexes are known that contain a ligand coordinated through a hard donor, typically oxygen or nitrogen [2]. We are interested in the coordination chemistry of amidate $[RC(O)NR']^-$and imidate $[RC(O)NC(O)R']^-$ ligands toward platinum(II) and use simple methods for their synthesis, using either Ag_2O in CH_2Cl_2, or a tertiary amine in methanol. Using these methods, complexes of various *N*-donor ligands including saccharin [3], 5,5-diethylbarbituric acid [4], 2-azetidinone [5], isatin (2,3-dihydroindole-2,3-dione) [6] and others [7], including metallacyclic complexes [8, 9] and isoelectronic gold(III) complexes [10, 11] have been synthesized and characterized.

In this contribution we report the synthesis and characterization of some new complexes of the six-membered ring 3,3-dimethylglutarimidate ligand, containing ancillary phosphine ligands. To date, no phosphine-containing complexes of this ligand have been reported; however, a number of mono- and di-nuclear platinum(II) complexes with *N*-donor ligands and either glutarimidate or 3,3-dimethylglutarimidate have been previously synthesized [12–17].

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2. Experimental

NMR spectra were recorded in $CDCl_3$ on a Bruker AVIII 400 instrument using Topspin 3.0 software; signals were referenced relative to residual non-deuterated solvent peaks, or external H_3PO_4 (for ^{31}P NMR spectra). Coupling constants are in hertz. ESI mass spectra were recorded on a Bruker MicrOTOF instrument, which was periodically calibrated using a solution of sodium formate. Samples of isolated products were prepared for analysis by dissolution in a few drops of dichloromethane followed by dilution with methanol and centrifugation. Assignment of ions was assisted by comparison of experimental and theoretical isotope patterns, the latter calculated using proprietary instrument-based software or an internet-based program [18]. M/z values are of the most abundant isotopomer in the isotope envelope of the ion. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. IR spectra were recorded as KBr discs on a Perkin Elmer Spectrum 100 FT-IR spectrometer.

Reactions were carried out in LR grade methanol, without exclusion of air, light, or moisture. Water was singly distilled prior to use. The following chemicals were used as supplied from commercial sources: 3,3-dimethylglutarimide (dmgH, Aldrich), sodium chloride (Ajax Chemicals), sodium bromide (BDH), and aqueous trimethylamine (BDH, 25–30% w/v). The complex *cis*-$[PtCl_2(PPh_3)_2]$ was prepared by addition of 2 mol equivalents of PPh_3 to $[PtCl_2(cod)]$ [19] (cod = 1,5-cyclo-octadiene) in dichloromethane, followed by precipitation of the product with petroleum spirits [20].

2.1. *Synthesis of cis-[PtCl(dmg)(PPh$_3$)$_2$] (1a)*

A mixture of *cis*-$[PtCl_2(PPh_3)_2]$ (378 mg, 0.478 mmol), 3,3-dimethylglutarimide (400 mg, 2.83 mmol), and sodium chloride (600 mg, large excess) in methanol (25 mL) with aqueous trimethylamine (2 mL) was refluxed for 90 min giving a very slightly cloudy, colorless solution. Water (70 mL) was added, initially dissolving the trace insoluble solid; further addition of water gave a white precipitate. After cooling to room temperature, the solid was filtered, washed successively with water (2×20 mL) and petroleum spirits (10 mL), and dried under vacuum to give **1a** (399 mg, 93%). Found: C, 57.77; H, 4.64; N, 1.64. $C_{43}H_{40}ClNO_2P_2Pt$ requires C, 57.67; H, 4.51; N, 1.56%. $^{31}P\{^1H\}$ NMR, δ 14.45 [d, $^1J(PtP) = 3986$ Hz, $^2J(PP) = 19$ Hz] and 7.66 [d, $^1J(PtP) = 3197$ Hz, $^2J(PP) = 19$ Hz]. A second minor species has δ 10.70 [d, $^1J(PtP) = 3446$ Hz, $^2J(PP) = 21$ Hz] and 9.54 [d, $^1J(PtP) = 3499$ Hz, $^2J(PP) = 21$ Hz]. ^1H NMR, δ 8.1–7.1 (m, Ph), 2.10 [d, H_a of CH_2, $^2J(H_aH_b) = 16$ Hz], 1.29 [d, H_b of CH_2, $^2J(H_aH_b) = 16$ Hz], 1.04 (s, Me), and 0.74 (s, Me). ESI MS: $[Pt(dmg)(PPh_3)_2]^+$ (m/z 859), $[PtCl(dmg)(PPh_3)_2 + Na]^+$ (m/z 918), $[2\{PtCl(dmg)(PPh_3)_2\} + Na]^+$ (m/z 1813).

2.2. *Synthesis of cis-[PtBr(dmg)(PPh$_3$)$_2$] (1b)*

A mixture of *cis*-$[PtCl_2(PPh_3)_2]$ (298 mg, 0.377 mmol), 3,3-dimethylglutarimide (467 mg, 3.31 mmol), and sodium bromide (800 mg, large excess) in methanol (25 mL) with aqueous trimethylamine (2 mL) was refluxed for 60 min giving a slightly cloudy, very pale yellow solution. Water (70 mL) was added, giving a white precipitate. After cooling to room temperature, the solid was filtered, washed with water (2×20 mL)

and petroleum spirits (10 mL), and dried under vacuum to give **1b** (315 mg, 89%). Found: C, 54.50; H, 4.31; N, 1.53. $C_{43}H_{40}BrNO_2P_2Pt$ requires C, 54.94; H, 4.29; N, 1.49%. $^{31}P\{^1H\}$ NMR, δ 14.59 [d, $^1J(PtP) = 3951$ Hz, $^2J(PP) = 17.5$ Hz] and 6.06 [d, $^1J(PtP) = 3179$ Hz, $^2J(PP) = 17.5$ Hz]. A minor impurity species has δ 10.7 and 7.8 but coupling constants could not be determined. ^1H NMR, δ 8.1–7.1 (m, Ph), 2.12 [d, H_a of CH_2, $^2J(H_aH_b) = 16$ Hz], 1.30 [d, H_b of CH_2, $^2J(H_aH_b) = 16$], 1.08 (s, Me), and 0.75 (s, Me). ESI MS: $[Pt(dmg)(PPh_3)_2]^+$ (m/z 859), $[PtBr(dmg)(PPh_3)_2 + Na]^+$ (m/z 962), $[2\{PtBr(dmg)(PPh_3)_2\} + Na]^+$ (m/z 1902).

2.3. *X-ray structure determination of cis-[PtCl(dmg)(PPh$_3$)$_2$] (1a)*

Crystals were obtained by vapor diffusion of diethyl ether into a dichloromethane solution at room temperature. X-ray data were collected on a Bruker Apex II CCD diffractometer at the University of Auckland and were corrected for absorption by a multi-scan method (SADABS) [21]. The structure was solved and refined with SHELX-97 [22]. The structure was solved by direct methods and developed routinely to give the two molecules of *cis*-$[PtCl(dmg)(PPh_3)_2]$ in the asymmetric unit. Subsequent difference maps revealed a molecule of diethyl ether and a partially occupied (0.75 occupancy) dichloromethane. The structure was refined in space group *Pn*, as a partial racemic twin (0.85 : 0.15). The symmetry of the higher space group *P*2/*n* was broken by the different solvent molecules in the asymmetric unit, although the two independent molecules showed *pseudo*-symmetry. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions. Crystal and refinement details are given in table 2.

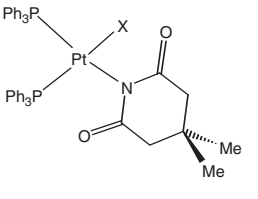
2.4. *Theoretical calculations*

The geometry of **1a** was optimized using the B3LYP density functional method with the 6-31G(d) basis set for the H, C, N, O, P, and Cl atoms and the LANL2DZ basis set and effective core potential for the Pt atoms. The initial geometry for optimization was taken from the corresponding X-ray crystal structure. The potential energy curve for rotation of the dmg was calculated by displacing the O–N–Pt–Cl dihedral angle from -180° to $+180^\circ$ in 10° increments with all other geometric parameters fixed at their optimized values. For the ^1H NMR calculations, the geometry of **1a** was re-optimized in dichloromethane using the integral equation formalism polarized continuum model. A solvated single-point NMR calculation was then run with the gauge-independent atomic orbital method using the B3LYP functional and 6-311++G(2d,2p) basis set for H, C, N, O, P, and Cl and the LANL2DZ basis set and effective core potential for Pt. Relative chemical shifts for **1a** were obtained by comparison to TMS calculated with the same theoretical approach. All DFT calculations were completed using Gaussian 09, Revision A.01 [23].

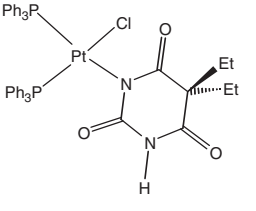
3. Results and discussion

The reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with an excess of 3,3-dimethylglutarimide and aqueous trimethylamine base in refluxing methanol gave a clear, colorless solution from

which a white solid product was recovered by precipitation with water. Analysis of the solid by positive-ion ESI mass spectrometry showed a single dominant ion at m/z 859.249, which is assigned to the mono-dmg species $[Pt(dmg)(PPh_3)_2]^+$ (calculated m/z 859.218), with good agreement between observed and calculated isotope patterns. However, analysis by ^{31}P NMR spectroscopy showed the presence of two products, each giving two doublets due to the presence of two inequivalent PPh_3 ligands with ^2J(PP) coupling. Thus, one product showed PPh_3 resonances at δ 14.45 and 7.66 showing ^1J(PtP) couplings of 3986 and 3197 Hz, respectively, while the second complex gave resonances at δ 10.70 and 9.54 showing ^1J(PtP) couplings of 3446 and 3499 Hz, respectively. In a number of attempts at forming a single product, reaction between *cis*-$[PtCl_2(PPh_3)_2]$, excess 3,3-dimethylglutarimide, and aqueous trimethylamine was repeated using different amounts of the imide, and different reaction times, however the same two products were always formed, in variable amounts. However, when the reaction between *cis*-$[PtCl_2(PPh_3)_2]$, excess 3,3-dimethylglutarimide, and aqueous trimethylamine was carried out in the presence of a large excess of sodium chloride, and the product precipitated with water, the product having ^{31}P NMR resonances at δ 14.45 and 7.66 was obtained in a fairly pure form, and subsequently characterized by NMR spectroscopy, ESI mass spectrometry, and a single-crystal X-ray structure determination as the mono-imidate complex *cis*-$[PtCl(dmg)(PPh_3)_2]$ (**1a**).



1a, X = Cl
1b, X = Br



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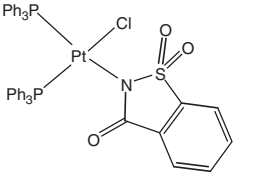

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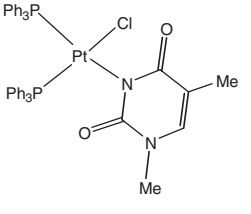

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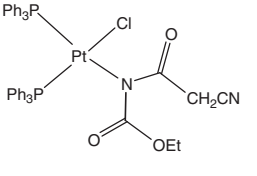

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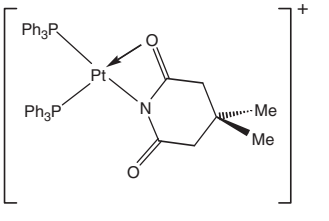

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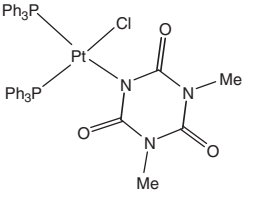

7

The ^{31}P NMR chemical shifts and ^{1}J(PtP) coupling constants for **1a** [δ 14.45 ($J = 3986$ Hz) and δ 7.66 ($J = 3197$ Hz)] are comparable to those of other closely related platinum(II) mono-imidate complexes of the type *cis*-[PtClL(PPh_3)$_2$] (L = imidate ligand), such as L = 5,5-diethylbarbiturate [**2**; δ 13.1 ($J = 3950$ Hz) and δ 6.6 ($J = 3337$ Hz)] [4], saccharinate [**3**; δ 15.2 ($J = 3770$ Hz) and δ 7.9 ($J = 3483$ Hz)] [3], 1-methylthyminate [**4**; δ 15.4 ($J = 3984$ Hz) and δ 8.6 ($J = 3235$ Hz)] [24], and N(CO_2Et)C(O)CH_2CN [**5**; δ 14.4 ($J = 3959$ Hz) and δ 7.1 ($J = 3330$ Hz)] [7]. The imidate ligand has a higher *trans*-influence (than chloride) [25], leading to a lower ^{1}J(PtP) coupling constant for the *trans* phosphorus.

The nature of the second component of the reaction mixture between *cis*-[$PtCl_2(PPh_3)_2$], 3,3-dimethylglutarimide, and Me_3N, having ^{1}J(PtP) values of 3446 and 3499 Hz, is less certain. One possibility is the *N*,*O*-chelated species **6**, although phosphines *trans* to low *trans*-influence oxygen donor ligands typically produce substantially larger values of ^{1}J(PtP) than those observed. The observation that crude samples of **1a**, containing both species yield a single ion in the ESI mass spectrum (*vide supra*) is consistent with **6**, although another species *cis*-[Pt(dmg)L(PPh_3)$_2$] would also be expected to give [Pt(dmg)(PPh_3)$_2$]$^+$ in the mass spectrum if L is significantly more labile than the dmg$^-$ ligand.

ESI MS analysis of isolated samples of **1a** (synthesized using added NaCl) in dichloromethane–methanol solution showed the ions [Pt(dmg)(PPh_3)$_2$]$^+$ (m/z 859), and [PtCl(dmg)(PPh_3)$_2$ + Na]$^+$ (m/z 918) as the most intense ions, together with the aggregate [2{PtCl(dmg)(PPh_3)$_2$} + Na]$^+$ (m/z 1813) formed from traces of Na^+ ions (presumably carried over from the synthesis). Increasing the capillary exit voltage increased the intensity of [Pt(dmg)(PPh_3)$_2$]$^+$. The preferential loss of the chloride ligand in ESI MS analysis is noteworthy, since it would presumably lead to the intramolecularly stabilized cationic species **6**. The same preferential loss of chloride was also observed for *cis*-[PtCl(debarb)(PPh_3)$_2$] (**2**) [4], but contrasts with the saccharin-derived complex **3** [3], where loss of both the chloride and saccharinate was observed. This difference may be due to the carbonyl (donor) group being part of a six-membered ring in **1a** and **2**, but a five-membered ring in the saccharinate complex **3**; the smaller ring would result in a less favorable bond angle upon coordination to platinum.

Table 1. Selected bond lengths (Å) and angles (°) for the two independent molecules of *cis*-[PtCl(dmg)(PPh_3)$_2$] (**1a**), with estimated standard deviations in parentheses.

Molecule 1		Molecule 2	
Pt(1)–N(1)	2.064(3)	Pt(2)–N(2)	2.067(3)
Pt(1)–P(2)	2.2335(13)	Pt(2)–P(3)	2.2306(13)
Pt(1)–P(1)	2.2847(10)	Pt(2)–P(4)	2.2813(11)
Pt(1)–Cl(11)	2.3447(13)	Pt(2)–Cl(21)	2.3359(14)
N(1)–C(15)	1.378(6)	N(2)–C(25)	1.362(6)
N(1)–C(11)	1.386(6)	N(2)–C(21)	1.386(6)
O(11)–C(11)	1.228(5)	O(21)–C(25)	1.225(5)
O(12)–C(15)	1.205(6)	O(22)–C(21)	1.225(6)
N(1)–Pt(1)–P(2)	90.37(11)	N(2)–Pt(2)–P(3)	89.76(11)
N(1)–Pt(1)–P(1)	171.34(11)	N(2)–Pt(2)–P(4)	170.60(11)
P(2)–Pt(1)–P(1)	97.15(4)	P(3)–Pt(2)–P(4)	98.03(4)
N(1)–Pt(1)–Cl(11)	85.07(11)	N(2)–Pt(2)–Cl(21)	85.06(11)
P(2)–Pt(1)–Cl(11)	172.74(4)	P(3)–Pt(2)–Cl(21)	171.62(4)
P(1)–Pt(1)–Cl(11)	87.86(4)	P(4)–Pt(2)–Cl(21)	87.77(4)

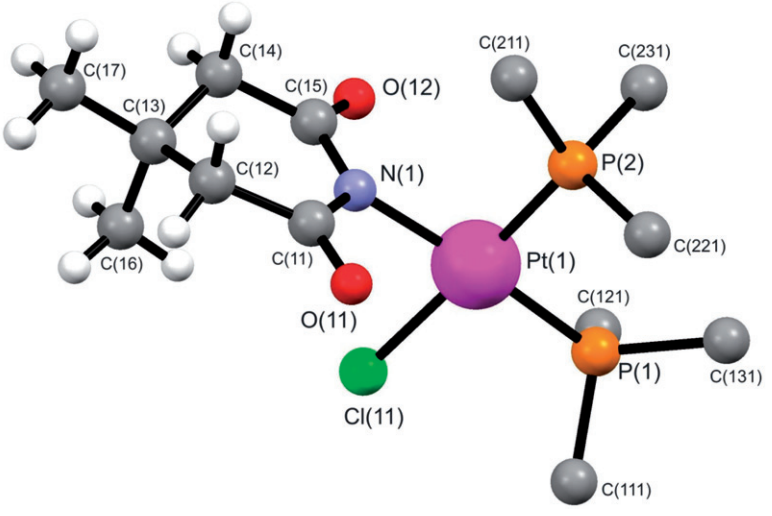

Figure 1. Molecular structure of one of the independent molecules of *cis*-[PtCl(dmg)(PPh_3)$_2$] (**1a**), showing the atom-labeling scheme. Only *ipso* carbon atoms of the triphenylphosphine ligands are shown for clarity.

Table 2. Crystallographic details for *cis*-[PtCl(dmg)(PPh_3)$_2$] (**1a**).

Formula	$C_{91}H_{92}Cl_4N_2O_5P_4Pt_2$
Molecular weight	1949.53
Temperature (K)	89(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*Pn*
Unit cell dimensions (Å, °)	
a	11.053(5)
b	24.309(5)
c	15.182(5)
β	94.208(5)
Volume (Å^3), *Z*	4068(2), 2
Calculated density (g cm^{-3})	1.591
Absorption coefficient (mm^{-1})	3.700
F(000)	1952
Crystal size (mm^3)	0.35 × 0.35 × 0.35
Reflections collected	51,951
Independent reflection	17,244 [$R_{int} = 0.0295$]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3575 and 0.3575
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	17,244/2/981
Goodness-of-fit on F^2	1.027
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0222$, $wR_2 = 0.0551$
R indices (all data)	$R_1 = 0.0232$, $wR_2 = 0.0555$
Absolute structure parameter	0.153(4)
Largest difference peak and hole (e Å^{-3})	1.250 and −0.589

In order to fully characterize *cis*-[PtCl(dmg)(PPh_3)$_2$] (**1a**), a single-crystal X-ray diffraction study was carried out. The complex crystallizes with two independent molecules in the unit cell, although there are only relatively minor differences between them. Selected bond lengths and angles for the two molecules are summarized in table 1, while the molecular structure of one of the independent molecules [molecule 1, containing Pt(1)] is shown in figure 1. There is also one molecule of dichloromethane and one molecule of diethyl ether co-crystallized in the lattice.

Bond distances and angles for the two independent molecules are typical for this type of complex. The previously reported saccharinate complex *cis*-[PtCl(sac)(PPh_3)$_2$] (**3**) [3], together with the recently reported platinum(II) complex **7** containing a 1,3-dimethylcyanurate ligand [26], provide good comparisons because of the presence of a single imidate ligand in each case. The Pt–N bond distances for the two molecules of **1a** [2.064(3) and 2.067(3) Å] are the same as in **3** and **7** [both 2.064(6) Å]; the Pt–Cl bond distances [Pt(1)–Cl(11) 2.3447(13), Pt(2)–Cl(21) 2.3359(14) Å] are likewise comparable to those in **3** [2.340(2) Å] and **7** [2.357(2) Å]. In **3**, the two Pt–P bond distances are the same [2.264(2) and 2.266(2) Å], while in **1a** there appears to be a significant difference between the two phosphines. Thus in molecule 1, the Pt–P bond lengths are Pt(1)–P(1) 2.2847(10) Å (*trans* to dmg) and Pt(1)–P(2) 2.2335(13) Å (*trans* to Cl). The corresponding bond lengths in molecule 2 are Pt(2)–P(4) 2.2813(11) Å (*trans* to dmg) and Pt(2)–P(3) 2.2306(13) Å (*trans* to Cl). Taken together, these data for the two independent molecules indicate that dmg has a higher *trans* influence, resulting in lengthening of the *trans* Pt–P bonds [to P(1) and P(4) in the two molecules]. The same effect is observed for the 1,3-dimethylcyanurate complex **7**, where the Pt–P bond *trans* to nitrogen [2.265(2) Å] is longer than the Pt–P bond *trans* to chloride [2.250(2) Å].

In both molecules of **1a** the platinum centers have the typical slightly distorted square-planar coordination geometry, with dihedral angles between the P–Pt–P and N–Pt–Cl planes of 7.13° and 8.43° in molecules 1 and 2, respectively. The dmg ligand adopts an arrangement that is almost perpendicular to the platinum coordination plane. Thus, in molecule 1, the dihedral angle between the least-squares coordination plane [Pt(1), P(1), P(2), N(1), Cl(11)] and the plane of the imidate part of the dmg ligand [as defined by atoms N(1), C(11), O(11), C(15) and O(12)] is 88.11°. The corresponding angle in molecule 2 is 85.03°. The same near orthogonality is also observed in the related saccharinate and 1,3-dimethylcyanurate complexes **3** and **7**, respectively.

The saturated [–$CH_2CMe_2CH_2$–] part of dmg is puckered out of the plane of the imidate part; this is a feature of 3,3-dimethylglutarimide itself [27], and of other derivatives thereof [15, 16]. Thus, N(1), C(11), O(11), C(15), O(12), C(14), and C(12) of molecule 1 are effectively co-planar, and the least-squares plane of this group is inclined at an angle of 47.47° to the plane defined by C(12), C(13), and C(14) of the $CH_2CMe_2CH_2$ moiety. Again, molecule 2 is similar, with a corresponding angle of 46.49°. This conformation places methyl groups in *pseudo*-axial and equatorial positions on the ring.

The near orthogonality of the platinum coordination and dmg planes, coupled with the puckering of the dmg ligand, results in one of the methyl C–H bonds being directed toward the coordinated chloride, although the long H···Cl distances [3.0747(6) and 3.1847(6) Å in molecules 1 and 2, respectively] preclude any significant interaction. There are also relatively short contacts between the platinum centers and the carbonyl oxygen atoms [e.g. in molecule 1, Pt(1)···O(11) 3.0787(6), Pt(1)···O(12) 3.0678(7) Å],

which are possibly very weak interactions [the sum of the van der Waals radii for Pt and O is 3.24 Å] [28].

To further investigate the structural features of **1a**, a computational study was carried out based on the geometry observed in the X-ray structure determination. The dmg was maintained in a rigid conformation and energies calculated upon rotation about the Pt–N bond. The lowest energy conformation was found to be when the C–N–Pt–Cl torsion angle was 90°, with the CMe_2 group directed toward the chloride, i.e., that observed structurally. Rotation of dmg through 180° (maintaining it in a rigid conformation) resulted in a higher energy structure as a result of steric interactions between the CMe_2 group and a PPh_3. As expected, local maxima resulted when the N–C–Pt–Cl torsion angle was 0° or 180°, where the dmg ligand was coplanar with the platinum coordination plane.

The ^{1}H NMR spectrum of **1a** showed inequivalence of both the CH_2 protons and the methyl groups of dmg. For the CH_2 protons, two AB doublets were observed at δ 2.10 and 1.29 showing mutual ^2J(HH) coupling of 16 Hz, while the methyl groups gave two singlets at δ 1.04 and 0.74. This inequivalence arises due to the dmg ligand adopting an arrangement perpendicular to the platinum coordination plane, which makes the two protons of each CH_2 group, and the methyl groups, inequivalent. Density functional theory (DFT) calculations indicate that the CH_2 protons (δ 2.15) and methyl protons (δ 1.10) on the side of the chloride ligand are downfield of the CH_2 protons (δ 1.55) and methyl protons (δ 0.79) on the side of a PPh_3 ligand. These observations are consistent with a lack of free rotation about the Pt–N bond due to the significant steric interactions between dmg and PPh_3 ligands.

Finally, reaction of *cis*-$[PtCl_2(PPh_3)_2]$, excess 3,3-dimethylglutarimide, sodium bromide, and aqueous trimethylamine gave the analogous bromo complex *cis*-$[PtBr(dmg)(PPh_3)_2]$ (**1b**), in high yield, and the $^{31}P\{^1H\}$ NMR spectrum showed the presence of one dominant product, with comparable parameters to **1a** [δ 14.59, ^1J(PtP) 3951 and δ 6.06, ^1J(PtP) 3179], together with traces of an impurity species as observed for **1a** (*vide supra*). Like **1a**, **1b** also showed inequivalence of the CH_2 and methyl protons of the dmg ligand, giving analogous ^{1}H NMR spectral features. Complex **1b** also gave ions formed by loss of halide in the ESI mass spectrum together with $[PtBr(dmg)(PPh_3)_2 + Na]^+$ and $[2\{PtBr(dmg)(PPh_3)_2\} + Na]^+$, analogous to the chloride complex.

In conclusion, we have synthesized two new platinum(II) complexes of the *N*-bonded 3,3-dimethylglutarimidate ligand; there are a number of similarities with the related 5,5-diethylbarbiturate system, specifically: (a) formation of a mono(imidate) complex (with an ancillary chloride ligand) by reaction of the ligand with *cis*-$[PtCl_2(PPh_3)_2]$, (b) mass spectrometric behavior (preferential ionization of chloride, and (c) structural characteristics (orthogonality of the coordination and imidate ligand planes).

Supplementary material

Crystallographic data for the structure described in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 864 526. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road,

Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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