

Synthesis and structural characterization of isomeric ‘lantern-shaped’ platinum(III) complexes of formula $[\text{Pt}_2(\text{PPh}_3)\text{X}\{N(\text{H})\text{C}(\text{R})\text{O}\}_4](\text{NO}_3)_2$ ($\text{X} = \text{PPh}_3, \text{H}_2\text{O}$)

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Abstract

The platinum(III) lantern type complexes $[\text{Pt}_2(\text{PPh}_3)_2\{N(\text{H})\text{C}(\text{R})\text{O}\}_4](\text{NO}_3)_2$ [$\text{R} = \text{Me}$ (**1**), Bu^t (**2**)], and $[\text{Pt}_2(\text{H}_2\text{O})(\text{PPh}_3)\{N(\text{H})\text{C}(\text{Bu}^t)\text{O}\}_4](\text{NO}_3)_2$ (**3**) were synthesized and characterized by ¹H NMR and X-ray crystallography (**2** and **3**). The compounds can give rise to formation of isomers differing for the sets of equatorial donor atoms around each platinum, $\text{N}^3\text{O}/\text{NO}^3$ or N^2O^2 , and, in the case of N^2O^2 , for the *cis* or *trans* geometry. The effect of the anion upon the chemical shifts of NH protons was studied for NO_3^- , BF_4^- , and ClO_4^- . The stability of phosphine axial ligands in the complexes $\text{N}^3\text{O}/\text{NO}^3$ - $[\text{Pt}_2(\text{PPh}_3)_2\{N(\text{H})\text{C}(\text{R})\text{O}\}_4](\text{NO}_3)_2$ as a function of the set of donor atoms was also studied. The complex $\text{N}^3\text{O}/\text{NO}^3$ -**3** is the first non-symmetric lantern-type platinum dimer to be characterized by X-ray diffraction. Comparison of the platinum/axial ligand bond distances in different complexes of this type allows to conclude that two factors contribute to the lengthening of axial bonds: the strong *trans* labilizing effect of the intermetallic bond and the *trans*-influence of the axial ligand on the second platinum unit.

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1. Introduction

Dinuclear platinum(III) complexes represent a topic of intense research not only from a theoretical point of view but also for their potential use in catalysis and biomedicine [1–4].

Starting from the early discovery of elusive platinum-blue materials [5], various types of amides and amidates have been used as terminal and bridging ligands, respectively [6]. In particular, terminal amide ligands were used for the synthesis of the first Pt(III) dimer unsupported by covalent bridges [7,8]. In spite of the great number of platinum(III) dimers supported by two amidate bridges ([1,2] and references therein) the

synthesis of platinum dimers with four bridging amidate ligands proved to be much more difficult and was accomplished only recently.

In a previous paper we reported the synthesis and X-ray structural characterization of $[\text{Pt}_2\text{Cl}_2\{N(\text{H})\text{C}(\text{Bu}^t)\text{O}\}_4]$, and made a comparison with the iodo analogue $[\text{Pt}_2\text{I}_2\{N(\text{H})\text{C}(\text{Me})\text{O}\}_4]$ [9]. A characteristic feature of platinum(III) dimers is an unusually long bond distance between the platinum and the axial ligands, which is approximately 10% longer than corresponding distances in square-planar platinum(II) and octahedral platinum(IV) species. Therefore, at least for dimeric species, the platinum(III) exhibit a binding affinity for axial ligands which can be considered intermediate between that of platinum(II) (very weak) and that of platinum(IV) (rather strong). A catalytic role has been envisaged for dimeric platinum(III) species which takes advantage of the possibility for the plati-

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num centers to assume, alternately, the properties typical of a platinum(II) or of a platinum(IV) substrate [2].

In order to further investigate the unusual properties of axial ligands in this rather unusual coordination environment we have extended the investigation to phosphine ligands which, like halide and amine ligands, are among the most widely studied ligands for coordination to platinum. As in the previous work the investigation has been extended to two types of bridging amides: acetamide and pivaloamide, two complexes, $[\text{Pt}_2(\text{PPh}_3)_2\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4](\text{NO}_3)_2$ (**2**) and $[\text{Pt}_2(\text{H}_2\text{O})(\text{PPh}_3)\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4](\text{NO}_3)_2$ (**3**), have also been characterized by X-ray crystallography.

2. Experimental

2.1. Syntheses

2.1.1. Starting materials

Reagent grade chemicals were used as received. $[\text{Pt}_2\text{I}_2\{N(\text{H})C(\text{Me})\text{O}\}_4]$ and $[\text{Pt}_2\text{Cl}_2\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4]$ were prepared as already described [9].

2.1.2. Preparation of $[\text{Pt}_2(\text{NO}_3)_2\{N(\text{H})C(\text{Me})\text{O}\}_4]$

$[\text{Pt}_2\text{I}_2\{N(\text{H})C(\text{Me})\text{O}\}_4]$ (200 mg, 0.23 mmol) was dissolved in $\text{C}_3\text{H}_6\text{O}$ (60 ml) and treated with a small excess of AgNO_3 (100 mg, 0.59 mmol) dissolved in water (2 ml). The reaction mixture was kept under stirring for approximately 2 h at 25 °C in the dark. The formed white precipitate (AgCl) was removed by filtration of the mother solution and the solvent evaporated to dryness in a rotary evaporator. The solid residue was dissolved in $\text{C}_3\text{H}_6\text{O}$ and the solution filtered on celite in order to remove the excess of AgNO_3 . The solvent was then evaporated to dryness in a rotary evaporator leaving a light green solid of the desired product. Yield: 135 mg (77%). *Anal.* Calc. for $[\text{Pt}_2(\text{NO}_3)_2\{N(\text{H})C(\text{Me})\text{O}\}_4]\cdot\text{H}_2\text{O}$: C, 12.6; H, 2.4; N, 11.0. Found: C, 12.4; H, 2.2; N, 10.4%.

2.1.3. Preparation of

$[\text{Pt}_2(\text{PPh}_3)_2\{N(\text{H})C(\text{Me})\text{O}\}_4](\text{NO}_3)_2$ (**1**)

$[\text{Pt}_2(\text{NO}_3)_2\{N(\text{H})C(\text{Me})\text{O}\}_4]$ (100 mg, 0.13 mmol) was dissolved in CHCl_3 (150 ml) and treated with an excess of PPh_3 (150 mg, 0.57 mmol). The reaction mixture was kept under stirring for approximately 6 h at 25 °C. The colour of the solution changed from light green to light orange. The solution was then evaporated to dryness in a rotary evaporator and the solid residue crystallized from CHCl_3 covered by a layer of C_5H_{12} . Orange crystals were formed. Yield: 101 mg (61%). *Anal.* Calc. for $[\text{Pt}_2(\text{PPh}_3)_2\{N(\text{H})C(\text{Me})\text{O}\}_4](\text{NO}_3)_2$: C, 41.6; H, 3.6; N, 6.6. Found: C, 41.1; H, 4.0; N, 6.3%.

2.1.4. Preparation of $[\text{Pt}_2(\text{NO}_3)_2\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4]$

$[\text{Pt}_2\text{Cl}_2\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4]$ (200 mg, 0.23 mmol) was dissolved in $\text{C}_3\text{H}_6\text{O}$ (40 ml) and treated with a small excess of AgNO_3 (100 mg, 0.59 mmol) dissolved in water (2 ml). The reaction mixture was kept under stirring for approximately 2 h at 25 °C in the dark. The formed white precipitate (AgCl) was removed by filtration of the mother solution which was then evaporated to dryness in a rotary evaporator. The solid residue was dissolved in CHCl_3 and the solution filtered on celite in order to remove the excess of AgNO_3 . The solvent was evaporated in a rotary evaporator leaving a light green solid of the desired product. Yield: 151 mg (70%). *Anal.* Calc. for $[\text{Pt}_2(\text{NO}_3)_2\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4]\cdot 0.5\text{CH}_3\text{COCH}_3$: C, 27.4; H, 4.6; N, 8.9. Found: C, 27.0; H, 4.5; N, 8.6%.

2.1.5. Preparation of

$[\text{Pt}_2(\text{PPh}_3)_2\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4](\text{NO}_3)_2$ (**2**) and of $[\text{Pt}_2(\text{H}_2\text{O})(\text{PPh}_3)\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4](\text{NO}_3)_2$ (**3**)

$[\text{Pt}_2(\text{NO}_3)_2\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4]$ (100 mg, 0.11 mmol) was dissolved in CHCl_3 (150 ml) and treated with an excess of PPh_3 (120 mg, 0.46 mmol). The reaction mixture was kept under stirring for approximately 4 h at 25 °C meanwhile the colour of the solution changed from light green to light orange. The solvent was evaporated in a rotary evaporator and the solid residue crystallized from a CHCl_3 solution covered by a layer of C_5H_{12} . Two types of crystals were obtained, most of them were orange [Yield: 106.8 mg (60%)] while a few were green [Yield: 6.6 mg (5%)]. *Anal.* Calc. for the orange crystals, $[\text{Pt}_2(\text{PPh}_3)_2\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4](\text{NO}_3)_2\cdot 1.5\text{CHCl}_3$ (**2**· 1.5CHCl_3): C, 42.7; H, 4.4; N, 5.2%. Found: C, 42.7; H, 4.5; N, 5.0%. *Anal.* Calc. for the green crystals, $[\text{Pt}_2(\text{H}_2\text{O})(\text{PPh}_3)\{N(\text{H})C(\text{Bu}^t)\text{O}\}_4](\text{NO}_3)_2$ (**3**): C, 38.2; H, 4.8; N, 7.0. Found: C, 38.1; H, 4.7; N, 6.4%.

2.2. X-ray crystal structure determination

Orange crystals of **1** were obtained by crystallization from $\text{CHCl}_3/\text{C}_5\text{H}_{12}$. X-ray data were collected by using a STOE IPDS four-circle diffractometer and most of the details of the structure analysis are listed in Table 1. Only the $C2$ space group yielded chemically reasonable results while the centric option (space group $C2/c$) gave unreasonable results. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques to locate all non-H atoms. During the refinement it became apparent that nitrate anions were suffering by high thermal parameters, moreover a Fourier-difference map revealed several maxima in the vicinity of the CHCl_3 molecule suggesting a positional disorder. Only Pt, P and Cl atoms were refined anisotropically, the remaining atoms necessitated isotropic treatment in order to maintain satisfactory thermal displacement parameters. Furthermore, in order

Table 1

Crystal data for $[\text{Pt}_2(\text{PPh}_3)_2\{N(\text{H})C(\text{Bu}^t)O\}_4](\text{NO}_3)_2 \cdot 2\text{CHCl}_3$ (**2**) and $[\text{Pt}_2(\text{H}_2\text{O})(\text{PPh}_3)\{N(\text{H})C(\text{Bu}^t)O\}_4](\text{NO}_3)_2$ (**3**)

| | | |
|--|---|---|
| Formula | $\text{C}_{58}\text{H}_{72}\text{Cl}_6\text{N}_6\text{O}_{10}\text{P}_2\text{Pt}_2$ | $\text{C}_{38}\text{H}_{57}\text{N}_6\text{O}_{11}\text{PPt}_2$ |
| Formula weight (g mol^{-1}) | 1678.0 | 1195.05 |
| Temperature (K) | 293 | 293 |
| Wavelength (\AA) | 0.71073 | 0.71073 |
| Crystal system | monoclinic | monoclinic |
| Space group | $C2$ | $P2_1/n$ |
| a (\AA) | 18.623(4) | 11.115(2) |
| b (\AA) | 15.565(3) | 21.198(4) |
| c (\AA) | 13.705(3) | 19.931(4) |
| β ($^\circ$) | 121.31(3) | 101.52(3) |
| Volume (\AA^3) | 3394(1) | 4601(2) |
| Z | 2 | 4 |
| Density (g cm^{-3}) | 1.642 | 1.725 |
| Absorption coef- ficient (cm^{-1}) | 44.6 | 61.7 |
| $F(000)$ | 1660 | 2344 |
| Crystal size (mm^3) | $0.30 \times 0.20 \times 0.15$ | $0.24 \times 0.16 \times 0.12$ |
| θ Max ($^\circ$) | 24 | 27.50 |
| Index ranges | $-18 \leq h \leq 17, -17 \leq k \leq 16, 0 \leq l \leq 15$ | $-14 \leq h \leq 14, 0 \leq k \leq 27, 0 \leq l \leq 25$ |
| Reflections col- lected | 3665 | 10 525 |
| Observed reflec- tions | 2968 | 5487 |
| Data/restraints/ parameters | 2968/0/157 | 5487/0/436 |
| Goodness-of-fit on F^2 | 1.023 | 0.782 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.055;$ $wR_2 = 0.131$ | $R_1 = 0.047;$ $wR_2 = 0.096$ |
| R indices (all data) | $R_1 = 0.072;$ $wR_2 = 0.143$ | $R_1 = 0.097;$ $wR_2 = 0.110$ |
| Scan mode | $\theta/2\theta$ | $\theta/2\theta$ |
| Largest peak (e \AA^{-3}) | 1.5 | 1.0 |
| Flack parameter | 0.00 | |

to ensure a good observations/parameters ratio, the phenyl groups were treated as rigid, idealized hexagons. Despite a reasonably R factor, the structure did not converge well and shift/e.s.d. values remained high throughout the refinement. The sample quality (for instance the diffraction peaks were rather broad) may account for these anomalies, along with the high residual electron density of $1.5 e \text{\AA}^{-3}$ lying approximately 1.2\AA from the Pt atom. Selected bond distances and angles are listed in Table 2. The estimated standard deviations are relatively high and thus the metrical data should be interpreted with caution.

Green crystals of **3** were also obtained by crystallization from $\text{CHCl}_3/\text{C}_5\text{H}_{12}$. Data were collected at room temperature, using a crystal of $0.24 \times 0.16 \times 0.12 \text{ mm}^3$ dimensions, on a Bruker–Nicolet R3m/V diffractometer in the θ range 3.5 – 27.5° , with graphite mono-

Table 2

Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{Pt}_2(\text{PPh}_3)_2\{N(\text{H})C(\text{Bu}^t)O\}_4](\text{NO}_3)_2$ (**2**)

| | | | |
|---------------------|----------|--------------|---------|
| <i>Bond lengths</i> | | | |
| Pt–PtA ^a | 2.504(1) | Pt–O(2) | 1.99(2) |
| Pt–P(1) | 2.460(4) | Pt–N(1) | 2.05(2) |
| Pt–O(1) | 2.06(2) | Pt–N(2) | 1.98(2) |
| <i>Bond angles</i> | | | |
| P(1)–Pt–PtA | 178.6(3) | P(1)–Pt–N(1) | 97.0(6) |
| N(1)–Pt–N(2) | 89.7(7) | P(1)–Pt–N(2) | 93.3(8) |
| N(1)–Pt–O(1) | 81.4(7) | P(1)–Pt–O(1) | 92.9(6) |
| N(1)–Pt–O(2) | 169.8(7) | P(1)–Pt–O(2) | 89.7(5) |
| N(2)–Pt–O(1) | 169.7(9) | PtA–Pt–N(1) | 84.4(6) |
| N(2)–Pt–O(2) | 97.7(9) | PtA–Pt–N(2) | 86.8(7) |
| O(1)–Pt–O(2) | 90.6(6) | PtA–Pt–O(1) | 87.2(5) |
| O(1)–C(1)–N(1A) | 118(3) | PtA–Pt–O(2) | 88.9(5) |
| N(2)–C(6)–O(2A) | 128(3) | | |

^a Symmetry operator: A $-x, y, 1-z$.

chromated Mo $K\alpha$ radiation. The crystal data and refinement parameters are summarized in Table 1. The structure was solved by heavy-atom methods, completed by subsequent Fourier syntheses, and refined with full-matrix least-squares methods on F^2 . A disorder was present involving a nitrate group. This was satisfactorily solved with two different positions (50:50 multiplicity) for the oxygen atoms resulting in a nearly regular oxygen hexagon around the N(6) atom.

Only the non-hydrogen atoms nearest to the Pt atoms were refined anisotropically and no attempt was made to locate the hydrogen atoms. The final difference map showed electron density peaks (up to $1.0 e \text{\AA}^{-3}$) in chemically unreasonable positions which were considered to be noise.

Selected interatomic distances and angles are shown in Table 3.

Table 3

Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{Pt}_2(\text{H}_2\text{O})(\text{PPh}_3)\{N(\text{H})C(\text{Bu}^t)O\}_4](\text{NO}_3)_2$ (**3**)

| | | | |
|---------------------|----------|-------------------|----------|
| <i>Bond lengths</i> | | | |
| Pt(1)–Pt(2) | 2.468(1) | Pt(2)–OW(1) | 2.279(6) |
| Pt(1)–P | 2.404(3) | Pt(2)–O(1) | 2.032(6) |
| Pt(1)–N(1) | 2.008(7) | Pt(2)–N(2) | 2.007(8) |
| Pt(1)–O(2) | 2.000(7) | Pt(2)–N(3) | 1.969(8) |
| Pt(1)–O(3) | 2.016(6) | Pt(2)–N(4) | 1.995(8) |
| Pt(1)–O(4) | 2.009(6) | | |
| <i>Bond angles</i> | | | |
| P–Pt(1)–Pt(2) | 176.3(1) | Pt(1)–Pt(2)–OW(1) | 178.8(2) |
| N(1)–Pt(1)–O(2) | 90.5(3) | O(1)–Pt(2)–N(2) | 90.7(3) |
| N(1)–Pt(1)–O(3) | 173.4(3) | O(1)–Pt(2)–N(3) | 175.2(3) |
| N(1)–Pt(1)–O(4) | 89.9(3) | O(1)–Pt(2)–N(4) | 89.0(3) |
| O(2)–Pt(1)–O(3) | 90.6(3) | N(2)–Pt(2)–N(3) | 91.1(3) |
| O(2)–Pt(1)–O(4) | 178.2(3) | N(2)–Pt(2)–N(4) | 173.3(3) |
| O(3)–Pt(1)–O(4) | 88.8(3) | N(3)–Pt(2)–N(4) | 88.7(3) |
| N(1)–C(1)–O(1) | 122.1(9) | N(3)–C(11)–O(3) | 123.2(9) |
| N(2)–C(6)–O(2) | 123.7(9) | N(4)–C(11)–O(4) | 124.5(9) |

All software is contained in the SHELXTL NT 5.10 program library [10].

2.3. Physical measurements

^1H and ^{31}P NMR 1D and 2D spectra were obtained with a Bruker Avance DPX 300WB spectrometer.

3. Results and discussion

3.1. $[\text{Pt}_2(\text{PPh}_3)_2\{\text{N}(\text{H})\text{C}(\text{Me})\text{O}\}_4](\text{NO}_3)_2$ (**1**)

The ^1H NMR spectrum of $[\text{Pt}_2(\text{PPh}_3)_2\{\text{N}(\text{H})\text{C}(\text{Me})\text{O}\}_4]^{2+}$ showed four signals in the region of methyl protons at 2.15, 2.05, 2.04, and 1.97 ppm. The intensity ratios between three signals (2.15, 2.05, and 1.97 ppm) were 1:2:1, respectively, moreover this intensity pattern remained constant in different samples while the ratio between this set of signals and the fourth signal at 2.04 ppm changed from sample to sample. Since the precursor of complex **1**, $[\text{Pt}_2\text{I}_2\{\text{N}(\text{H})\text{C}(\text{Me})\text{O}\}_4]$, was a mixture of two isomers (N^2O^2 and $\text{N}^3\text{O}/\text{NO}^3$) [9], it is likely that the same mixture of isomers is present in the bisphosphine derivative. Therefore, the signals at 2.15, 2.05, and 1.97 ppm were assigned to the $\text{N}^3\text{O}/\text{NO}^3$ isomer of **1** for which only two, out of the four acetamidate ligands, are equivalent, while the signal at 2.04 ppm was assigned to the N^2O^2 isomer for which all four acetamidate ligands are equivalent.

Four signals were observed also in the NH region. The NH signals showed a small coupling with ^{31}P , consequently a ^{31}P decoupled spectrum was registered for the precise determination of the NH signals which fall at 7.08, 6.04, 5.66, and 5.31 ppm. The intensity ratios

between the signals at 7.08, 5.66, and 5.31 ppm were 2:1:1, respectively, and were constant in different samples, while the intensity of the peak at 6.04 ppm, with respect to the previous set of three signals, changed from sample to sample. Therefore, it is most likely that the set of three signals belongs to the $\text{N}^3\text{O}/\text{NO}^3$ isomer while the fourth signal at 6.04 ppm belongs to the symmetrical N^2O^2 isomer. A NOESY experiment confirmed that the three methyl signals at 2.05, 2.15, and 1.97 ppm are correlated with the three NH signals at 7.08, 5.66, and 5.31 ppm, while the NH signal at 6.04 ppm is correlated with the methyl signal at 2.04 ppm (Fig. 1).

In the $\text{N}^3\text{O}/\text{NO}^3$ isomer, the NH protons *trans* to oxygen exhibit a $^{31}\text{P}-^1\text{H}$ coupling of 4 Hz, while the NH protons *trans* to another NH, exhibit a $^{31}\text{P}-^1\text{H}$ coupling of 2.5 Hz. The different values of $J(^{31}\text{P}-^1\text{H})$ are in accord with a smaller *trans* influence of oxygen with respect to nitrogen donors. The ^1H NMR spectra of the symmetrical isomer would also be in accord with a N^4/O^4 configuration, instead of N^2O^2 , however, X-ray and ^{31}P NMR data for the analogous isomer of compound **2** rule out the N^4/O^4 configuration.

The $\text{N}^3\text{O}/\text{NO}^3$ isomer of **1** is stable in chloroform solution if an excess of triphenylphosphine is present. In contrast, in the absence of excess PPh_3 , it tends to decompose forming a white precipitate. This procedure was used for isolating the pure *cis*- N^2O^2 -isomer (which is stable in the absence of excess of PPh_3) from the mixture of the $\text{N}^3\text{O}/\text{NO}^3$ and N^2O^2 isomers. We could also prove that the white precipitate redissolves in the presence of excess PPh_3 , affording the original $\text{N}^3\text{O}/\text{NO}^3$ bisphosphine derivative. We hypothesize that the $\text{N}^3\text{O}/\text{NO}^3$ -bisphosphine derivative undergoes substitution of one phosphine from a nitrate anion forming $[\text{Pt}_2(\text{NO}_3)(\text{PPh}_3)\{\text{NHC}(\text{Me})\text{O}\}_4](\text{NO}_3)$ which is less so-

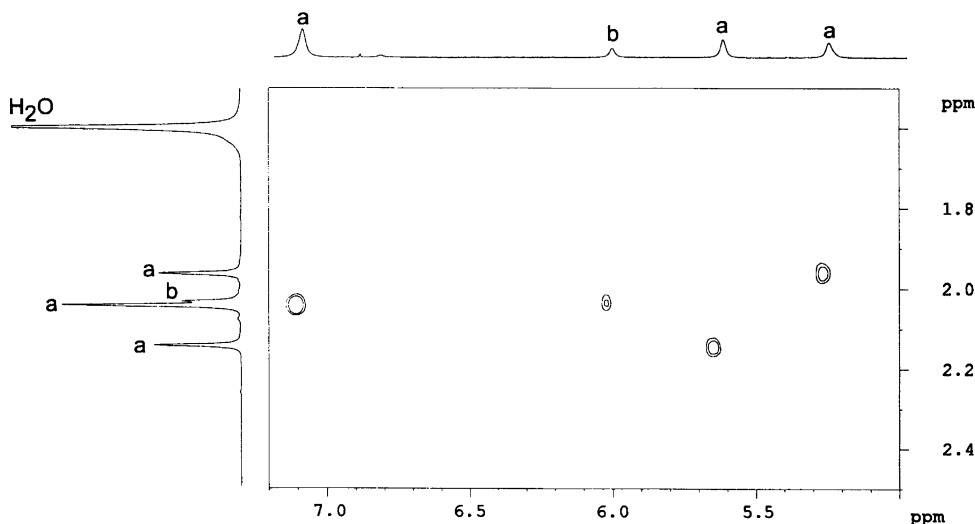
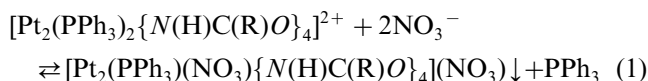


Fig. 1. NOESY spectrum and ^{31}P decoupled 1D ^1H spectrum of $[\text{Pt}_2(\text{PPh}_3)_2\{\text{N}(\text{H})\text{C}(\text{Me})\text{O}\}_4](\text{NO}_3)_2$ (**1**) in CDCl_3 solution. The signals of the $\text{N}^3\text{O}/\text{NO}^3$ isomer were labelled with a, while those of *cis*- N^2O^2 isomer were labelled with b.

luble in chloroform, having only one lipophilic PPh₃ ligand, and precipitates as a white solid (Eq. (1)).



In order to prove the above hypothesis we synthesized the same bisphosphine compound with a non coordinating counter ion (ClO₄⁻ or BF₄⁻). As expected the bisphosphine compound was stable even in the absence of excess triphenylphosphine. We could also notice that the chemical shifts of the NH protons are strongly affected by the nature of the counter ion. For instance substitution of BF₄⁻ for NO₃⁻ causes the chemical shifts of the NH protons at 7.08, 5.66, and 5.31 ppm to be shifted at 6.26, 4.82 and 4.84 ppm, respectively. The shift is greater for the NH's of the N³O–platinum-subunit (0.82–0.84 ppm) than for the NH of the NO³ subunit (0.47 ppm). The shift of the NH signals was even greater when the nitrate anion was replaced by perchlorate (new signals at 5.95, 4.78, and 4.71 ppm, respectively). The deshielding effect of the nitrate anion, with respect to perchlorate and tetrafluoroborate anions, is indicative of a greater ability of the NO₃⁻ anion to give H-bond interactions with the NH's. Such an interaction could be favoured by the planar shape of the nitrate anion which can interact with the NH hydrogen atoms without severe steric clash with the PPh₃ ligand. This would not be possible for perchlorate and tetrafluoroborate having a tetrahedral geometry. The greater downfield shift of the NH's of the N³O–Pt subunit with respect to the NO³–Pt subunit could be a consequence of the nitrate anions concentrating around the former subunit.

3.1.1. [Pt₂(PPh₃)₂{N(H)C(Bu^t)O}₄](NO₃)₂ (2) and [Pt₂(H₂O)(PPh₃)₂{N(H)C(Bu^t)O}₄](NO₃)₂ (3)

Complex **2** was investigated by ¹H NMR spectroscopy in CDCl₃. Four signals (1.08, 0.96, 0.91, and 0.89 ppm) were observed in the region of *tert*-butyl groups. The intensity ratios of signals at 1.08, 0.91, and 0.89 ppm were 1:2:1, respectively, and remained constant in different samples while the relative intensity of the fourth signal changed from sample to sample. Three signals were observed in the region of NH protons (6.88, 5.86, and 4.77 ppm). The NH signals at 6.88 and 4.77 ppm (intensity ratio 2:1) showed a small coupling with ³¹P, consequently a ³¹P decoupled spectrum was registered in order to better evaluate the chemical shifts and intensities of the NH signals. The signal at 5.86 ppm did not change in the ³¹P decoupled spectrum with respect to the coupled one. The NOESY spectrum revealed the existence at a fourth NH's signal at 5.84 ppm and overlapping with the signal at 5.86. Moreover, it indicates that the Bu^t signals at 1.08, 0.91, and 0.89 ppm (intensity ratios 1:2:1) are correlated with the NH

signals at 5.84, 6.88, and 4.77 ppm, respectively, while the NH signal at 5.86 ppm correlates with the Bu^t signal at 0.96 ppm. Therefore, two isomers are present in solution: one symmetrical with N²O² donor atoms around the two platinum atoms (*tert*-butyl signal at 0.96 ppm and NH signal at 5.86 ppm) and one non-symmetrical with N³O donor atoms around one platinum atom and NO³ donor atoms around the second platinum atom (*tert*-butyl signals at 1.08, 0.91, and 0.89 ppm and NH signals at 5.84, 6.88, and 4.77 ppm). As already observed for the acetamidate complex **1** also the N³O/NO³ isomers of **2** is unstable in the absence of excess triphenylphosphine and, while its proton NMR signals decrease in intensity, three new signals rise at 1.21, 1.04, and 0.90 ppm (intensity ratios 1:2:1). The new signals belong to a new compound which is formed from **2** by substitution of a phosphine ligand by a water molecule, N³O/NO³–[Pt₂(H₂O)(PPh₃)₂{N(H)C(Bu^t)O}₄](NO₃)₂ (**3**). The new compound was obtained in crystalline form and its structure was determined by X-ray diffraction. Complex **3** is the first non-symmetric N³O/NO³ lantern-type platinum dimer with four bridging amidate ligands to be characterized by X-ray diffraction.

Similarly to the acetamide system, also for the pivaloamide system the dissociation of an apical phosphine is a reversible process. Therefore, complex **3** in the presence of an excess of triphenylphosphine reverts to complex **2**.

Similarly to complex **1**, also in the case of **2**, substitution of ClO₄⁻ for NO₃⁻ deeply influences the NMR spectrum in CDCl₃ solution. Thus substitution of ClO₄⁻ for NO₃⁻ causes a shift of the NH signals from 6.88, 5.86, 5.84, and 4.77 ppm to 5.86, 5.21, 5.09, and 4.63 ppm, respectively. For the N³O/NO³ isomer the shift is greater for NH's of the N³O subunit (1.02–0.63 ppm) than for the NH of the NO³ subunit (0.14 ppm), while for the *cis*-N²O² isomer the shift of the NH signal is 0.77 ppm.

Differently from the N³O/NO³ isomer which is stable in the presence of excess PPh₃ (and unstable in the absence of free phosphine), the *cis*-N²O² isomer is unstable in CHCl₃ solution, and decomposes in an irreversible way, if free triphenylphosphine is present in excess. The rate of decomposition is greater if the concentration of free phosphine is higher.

The {¹H}³¹P spectra showed a signal at –5.5 ppm for the *cis*-N²O² isomer of **2**, two signals at –1.0 and –9.6 ppm for the N³O/NO³ isomer of **2**, and a signal at 30.6 ppm for complex **3**. The presence of only one ³¹P signal (–5.5 ppm) for the symmetrical isomer of **2** is in accord with a N²O² configuration and rules out the N⁴/O⁴ configuration which could be compatible with the ¹H NMR data.

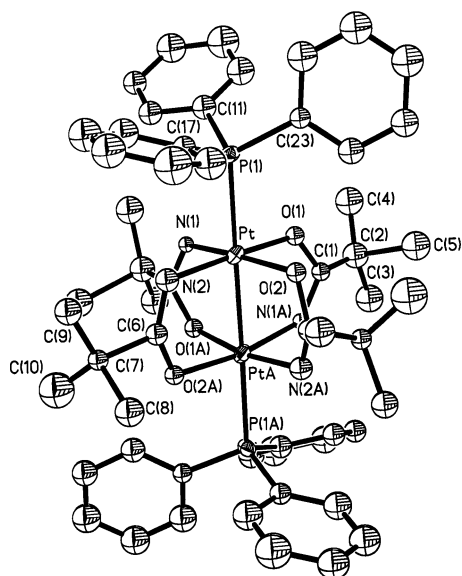


Fig. 2. View of the complex molecule $cis\text{-N}_2\text{O}_2\text{-}[\text{Pt}_2(\text{PPh}_3)_2\{\text{N}(\text{H})\text{C}(\text{Bu})\text{O}\}_4]^{2+}$ ($cis\text{-N}_2\text{O}_2$ isomer of **2**). The suffix A denotes atom at $-x, y, 1-z$.

3.1.2. Crystal structure of **2**

The crystal structure of **2** was investigated by X-ray analysis. The asymmetric unit comprises half a molecule of the $[\text{Pt}_2(\text{PPh}_3)_2\{\text{N}(\text{H})\text{C}(\text{Bu})\text{O}\}_4](\text{NO}_3)_2 \cdot 2\text{CHCl}_3$ compound and the overall structure is generated by the twofold axis (Fig. 2). Each of the platinum(III) atoms has a distorted octahedral geometry with the PPh_3 and the second platinum subunit in axial positions. The platinum atom is displaced from the mean equatorial N^2O^2 plane by 0.11 \AA towards the phosphorus donor. The four donor atoms deviate only slightly (0.01 \AA) from the mean equatorial plane. The five-membered $\text{Pt}(1)\text{-N-C-O-Pt}(2)$ rings (the suffix A denotes the symmetry-related atom at $-x, y, 1-z$) are roughly planar (maximum deviation $\leq 0.11 \text{ \AA}$), and orthogonal to each other (dihedral angles of 89.3 and 90.7°).

The bond length between the axial phosphine and the platinum atom (2.460 \AA) is much greater than analogous bond distances in four-coordinate platinum(II) complexes which fall in the range $2.24\text{--}2.30 \text{ \AA}$ [1–14]. The lengthening of the axial bond is a common feature of platinum(III) dimers and has been ascribed to a very strong *trans*-influence exerted by the intermetallic bond [7,8]. However, also the axial ligand on the second platinum unit is likely to exert a *trans*-influence which should be transmitted through a sequence of three bonds and not of only two bonds as in the usual case of mononuclear complexes. This second contribution will appear clear in compound **3** characterized by having axial ligands of different *trans*-influence [15].

In the crystal the molecules interact with neighbouring molecules via normal van der Waals contacts. The

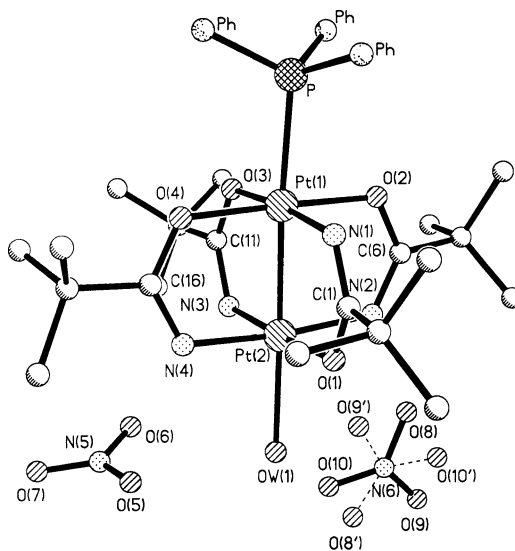
only short contact (2.93 \AA) involves the N(2) atom and the O(3) atom of the neighbouring nitrate anion ($\text{N-H}\cdots\text{O}$ angle of 106.21°). The existence of such an interaction supports the view that in CDCl_3 solution the flat molecule of nitrate is able to H-bond the N–H protons causing a downfield shift of the corresponding signals of approximately 1 ppm. The ClO_4^- and BF_4^- anions, because of their tetrahedral geometry, are found to be much less effective in giving this type of interaction.

3.1.3. Crystal structure of **3**

Also the $[\text{Pt}_2(\text{H}_2\text{O})(\text{PPh}_3)\{\text{N}(\text{H})\text{C}(\text{Bu})\text{O}\}_4](\text{NO}_3)_2$ compound (**3**) was investigated by X-ray analysis. In this case the asymmetric unit comprises one molecule of substrate (Fig. 3).

The coordination geometry of each platinum(III) atom can be considered a distorted octahedron. One platinum atom is displaced from the mean equatorial N^3O plane by 0.10 \AA towards the axial water molecule while the second platinum is displaced from the mean equatorial NO^3 plane by 0.07 \AA towards the phosphine ligand. The smaller displacement from the equatorial plane of the platinum atom in the NO^3 subunit correlates with the Pt–Pt distance which is shorter in compound **3** ($2.468(1) \text{ \AA}$) than in compound **2** ($2.504(1) \text{ \AA}$). The difference in Pt–Pt bond length between **2** and **3** is a consequence of the smaller *trans*-influence of the axial water molecule as compared to PPh_3 . The five-membered $\text{Pt}(1)\text{-N-C-O-Pt}(2)$ rings are roughly planar (maximum deviation $\leq 0.03 \text{ \AA}$) and orthogonal to each other (dihedral angles in the range $91.4\text{--}88.8^\circ$).

The bond length between the axial oxygen donor and the corresponding platinum atom ($2.279(6) \text{ \AA}$) is much longer than analogous bond distances in platinum(II)



complexes. For instance in the platinum complex *trans*-[Pt{HN=C(O)Bu¹}₂(H₂O)₂]:1/3H₂O the Pt–O bond distances were 2.016(7) Å and the water ligands were *trans* to oxygen-donor ligands [16]. Slightly longer Pt–O distances were found in the complexes *cis*-[Pt(H₂O)(NH₃)₂(1-methylcytosine-*N*³)](NO₃)₂·H₂O, [Pt(H₂O)(SO₄)₂{1,1-bis(aminomethyl)cyclohexane}]·H₂O, and [Pt(H₂O)(SO₄)₂{*N,N'*-dimethylethylenediamine}]·H₂O (average value 2.08 Å) where the water ligands are *trans* to nitrogen-donor ligands [17]. Within Pt(III) lantern-type compounds, axial Pt–O bond distances were found to be 2.11(1) Å for [Pt₂(SO₄)₄(H₂O)₂]²⁻ and 2.16(1) and 2.14(1) Å for [Pt₂(HPO₄)₄(H₂O)₂]²⁻ [8–19]. The Pt–O lengthening observed in complex **3** with respect to analogous Pt(III) dimers, can be ascribed to the strong *trans* influence exerted by the *trans* phosphine ligand. It is to be noted that the *trans*-influence, that in the present case is transmitted through three bonds and not through two bonds, as in the usual case, does not appear to be attenuated by the presence of the extra bond. The Pt–P distance of 2.404(3) Å, although longer than analogous bond distances in four-coordinate platinum(II) complexes, is shorter than that observed in compound **2** (2.460 Å). The approximately 0.05 Å difference between Pt–P bond distances in the two complexes is to be ascribed to a second-order effect, that is the *trans*-influence of the axial ligand on the second platinum unit which is a water molecule in **3** and a second phosphine ligand in **2** [11].

In the crystal both nitrate anions are positioned close to the platinum subunit carrying the axial water molecule. This positioning allows the oxygen atoms of the nitrate groups to interact with a major number of protons (NH groups and axial water molecule). Moreover, in this situation the nitrate does not suffer steric clash with the phosphine ligand which instead would be present if the nitrate was interacting with NH groups of the other platinum subunit.

3.2. Conclusions

A characteristic feature of platinum(III) dimers is the unusually long distances between the platinum centers and the axial ligands. Therefore, the binding affinity of axial ligands for this type of complexes can be considered intermediate between that of platinum(II) (very weak) and that of platinum(IV) substrates (very strong). A catalytic role has been envisaged for dimeric platinum(III) dimers which takes advantage of the possibility for the platinum centers to assume, alternately, the properties typical of a platinum(II) or of a platinum(IV) substrate [2]. In the case of amidate bridging ligands the donor atoms can be arranged in different ways about the two platinum centers, with the consequence that the reactivity of the two platinum subunits can be different.

This problem has seldom been considered in the past [18,20].

We have demonstrated in the case of acetamidate and pivaloamidate bridging ligands that two different arrangements of donor atoms around platinum are preferred: *cis*-N²O² and N³O/NO³. In the case of *cis*-N²O² donors, the complex is symmetrical while in the case of N³O/NO³ one platinum has three nitrogen and one oxygen donors while the second platinum has one nitrogen and three oxygen donor atoms. In the case of phosphine axial ligands the stability of the complexes depends upon the set of donor atoms. Hence in chloroform solution, the *cis*-N²O² isomer is stable, while the N³O/NO³ isomer is stable only in the presence of excess phosphine. In the absence of excess phosphine one PPh₃ ligand is selectively displaced from the N³O subunit forming a new species in which the axial position is kept by a nitrate or a water molecule. It is most likely that the driving force in this reaction is the greater affinity of the nitrate anions for the NO³ subunit.

Formation of hydrogen bonds between the nitrate anions and the amidic nitrogens has been observed in the X-ray structure of N³O/NO³-[Pt₂(H₂O)(PPh₃)-{*N*(H)C(Bu¹)O}₄](NO₃)₂. Moreover, in solution, the chemical shifts of the N–H protons of compounds **1** and **2** are strongly influenced by the nature of the counter ion. The nitrate anion causes a downfield shift of 0.6–1.1 ppm for the NH protons of the N³O set and of 0.1–0.5 ppm for the NO³ set of donor atoms. The downfield shift for the *cis*-N²O² arrangement is approximately 0.80 ppm. All these observations support the view that H-bonds are formed between amidic protons and nitrate anions and that the overall effect (strength of the H-bonds and/or number of interacting nitrates) is greater for the N³O subunit. The reaction of release of the phosphine ligand is reversible and in the presence of excess of PPh₃ the bisphosphine adduct is restored.

For the first time a non-symmetrical amidate-bridged dimer has been characterized by X-ray crystallography. The presence of different ligands in axial positions has allowed to conclude that two factors contribute to the lengthening of the platinum/axial ligand bond distance: the strong *trans* labilizing effect of the intermetallic bond and the *trans*-influence of the axial ligand on the second platinum unit. The intermediacy of three bonds, instead of the two bonds present in mononuclear systems, does not appear to attenuate the *trans*-influence of the axial ligand on the second subunit.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 194228 and 194229 for compounds **2** and **3**. Copies of this information may

be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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