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# The X-ray Structure of *cis*-Bis(cyclopropylamine)bis(1-methylthyminato-$N^3$)-platinum(II) Dihydrate, *cis*-$(cpa)_2Pt(1\text{-}MeT)_2 \cdot 2H_2O$, and Chemistry Related to 'Platinum Thymine Purple'

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## Abstract

The crystal structure of *cis*-$(cpa)_2Pt(1\text{-}MeT)_2 \cdot 2H_2O$ (**1**) with cpa = cyclopropylamine and 1-MeT = 1-methylthymine anion ($C_6H_7N_2O_2$), is reported, **1** crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 10.645(2)$, $b = 14.878(3)$, $c = 15.535(3)$ Å, $\beta = 106.44(3)°$, $V = 2359.8$ Å$^3$, $Z = 4$. Pt coordination to the 1-MeT rings is through N3 each with the two 1-MeT rings oriented head–head. Thus **1** can be considered a realistic model of a hypothetical cross-link of two thymine bases of DNA by a *cis*-$a_2Pt(II)$ moiety. As shown by $^1H$ NMR spectroscopy, **1** loses both cpa and 1-MeT ligands in acidic medium. Likewise, *cis*-$(cpa)_2PtCl_2$ undergoes solvolysis in aqueous solution with liberation of cpa. Starting with **1**, dinuclear complexes of composition *cis*-$[(cpa)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2]^{2+}$ (**2**), *cis*-$[(cpa)_2Pt(1\text{-}MeT)_2Pt(cpa)_2]^{2+}$ (**3**) and *cis*-$(cpa)_2Pt(1\text{-}MeT_2\text{-}PtCl_2$ (**4**), as well as a purple, mixed-valence compound of unknown composition were prepared. The 'purple', which originally was derived from *cis*-$(cpa)_2PtCl_2$ and 1-methylthymine, was reinvestigated and, based on ESCA data, is assigned a Pt oxidation state between 2 and 3 rather than 3.75 as proposed before.

## Introduction

Intensely colored Pt complexes of pyrimidine nucleobases (thymine, uracil, cytosine) [1] and related cyclic amides [2–4] have attracted considerable attention in recent years as a consequence of interesting pharmacological and chemical properties. Among the large number of green, blue, purple and red Pt compounds described so far, only two types are structurally characterized: tetranuclear complexes with a dimer-of-dimer structure and Pt(2.25) [2, 5] and Pt(2.5) [3a] average oxidation states**, and a trinuclear, mixed-metal $Pt_2Pd$ complex with a metal +2.33 average oxidation state [6]. A third type, consisting of Cl-bridged dinuclear $Pt_2$ units and +2.5 average oxidation state [7] is under active investigation in our laboratory. All structurally characterized examples contain *cis*-$(NH_3)_2Pt$ or (en)Pt entities, but it has become evident [5] that the en ligand, most likely because of its bulkiness compared to two $NH_3$ groups, is less willing to form 'blues'. Considering this result, formation of a purple 1-methylthymine complex derived from *cis*-(cyclopropylamine)$_2PtCl_2$, as reported by Thomson *et al.* in 1977 [8], is certainly remarkable. Except for an EXAFS study [9] on $(cpa)_2Pt(II)$/uridine, no further studies have been conducted to our knowledge. We therefore decided to reinvestigate the $(cpa)_2Pt(II)$/1-MeT system.

## Experimental

### Preparations

*cis*-$(cpa)_2PtCl_2$ and *cis*-$(cpa)_2PtI_2$ (cpa = cyclopropylamine) were prepared from $K_2PtCl_4$ according to the method of Howard-Lock *et al.* [10] and recrystallized from $H_2O$ and MeOH respectively. Preparation of *cis*-$(cpa)_2PtCl_2$ according to the method of Connors *et al.* [11] gave only low yields.

The title compound *cis*-$(cpa)_2Pt(1\text{-}MeT)_2 \cdot 2H_2O$ (**1**) was prepared by reacting 2 mmol of *cis*-$[(cpa)_2Pt(H_2O)_2](NO_3)_2$, in 30 ml $H_2O$, obtained *in situ* from *cis*-$(cpa)_2PtI_2$ with the use of $AgNO_3$, with 8 mmol 1-MeTH and 4 mmol NaOH in 30 ml $H_2O$ for 3 days at 60 °C. The solution was concentrated to a

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**See 'Note Added in Proof' p. 130.

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small volume by rotary evaporation at 22 °C, filtrated from unreacted 1-MeTH and purified via Sephadex (G-10-120) chromatography. The mixture, consisting of white microcrystals and a brownish precipitate, was recrystallized from water. Yield 70%. Slow evaporation at room temperature over four weeks gave colourless transparent single crystals of **1** suitable for X-ray crystallography. Yield 30%. *Anal.* Calc. for $PtC_{18}H_{32}N_6O_6$: C, 34.67; H, 4.52*; N, 13.47. Found: C, 34.55; H, 4.52; N, 13.36%.

The dinuclear complexes of **2** and **3** were prepared following the general route [12] of reacting *cis*-$X_2PtL_2$ with *cis*-$[Y_2M(H_2O)_2]Z_2$. No attempts were made to optimize yields.

*cis*-$[(cpa)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2](NO_3)_2 \cdot H_2O$ (**2**). Reaction conditions: 12 h, 22 °C, evaporation to a small volume by rotary evaporation at 22 °C and precipitation with $NaNO_3$ gave a greyish powder. Yield 20%. *Anal.* Calc. for $Pt_2C_{18}H_{36}N_{10}O_{11}$: C, 22.55; H, 3.78; N, 14.61. Found: C, 22.4; H, 3.7; N, 14.4%.

*cis*-$[(cpa)_2Pt(1\text{-}MeT)_2Pt(cpa)_2]X_2 \cdot NaX$ (**3**) ($X = NO_3^-$ or $ClO_4^-$). Reaction conditions: 4–5 days, 22 °C, evaporation to a small volume by rotary evaporation at 22 °C and precipitation with NaX gave a bluish powder of **2** containing NaX. *Anal.* Found for $ClO_4^-$ salt: C, 23.55; H, 3.18; N, 9.02% gives C:N = 2.58. Calc. for dinuclear complex C:N = 2.57.

*cis*-$(cpa)_2Pt(1\text{-}MeT)_2PtCl_2 \cdot 8.5H_2O$ (**4**) was prepared in an analogous way as $a_2Pt(1\text{-}MeT)_2PtCl_2$ [13] by reacting an aqueous solution of **1** with an equivalent of $K_2PtCl_4$. A small amount of a dark precipitate was filtered off and discarded. Slow evaporation at room temperature gave a brownish-black precipitate. Yield 13%. *Anal.* Calc. for $Pt_2C_{18}H_{45}N_6O_{12.5}Cl_2$: C, 21.40; H (dehydrated sample*), 2.60; N, 8.50. Found: C, 21.48; H (dehydrated sample*), 2.80; N, 8.35%.

The purple platinum complex was prepared according to Thomson *et al.* [8]. The authors did not comment on the yield but according to our experience the yield is less than 1%.

### *Physical Measurements*

IR spectra were recorded on Perkin-Elmer 783 and 580 B spectrometers, FT-IR spectra were recorded on a Bruker spectrometer, Type IFs 113v. $^1H$ NMR spectra were recorded on the following instruments: Varian EM 360 A, Bruker WM 250 and AM 300. NMR samples were measured as $D_2O$ solutions ($NMe_4^+$ as internal standard, referenced to sodium 3-(trimethylsilyl)propanesulfonate). UV–Vis spectra were recorded on Perkin-Elmer 555 and Lambda 15 instruments. pH values were measured by use of a glass electrode (Methrom). For $D_2O$ solution, 0.4 unit was added to the meter reading. For the $pK_a$ determination, uncorrected pH* values were taken.

Elemental analysis by scanning electron microscopy was carried out with a Cambridge Instruments Stereoscan S 150 or 360, using an analytical unit EDAX Model 711 or Link EDX. C, H, N analysis data were obtained by use of Lazlo Erba Strumentazione 116 and Perkin-Elmer 240 instruments.

The X-ray photoelectron spectroscopic measurements were obtained with a VG Scientific Instruments ESCA spectrometer using Al Kα radiation (1486.6 eV) as the X-ray excitation source. The powdered sample was dusted onto double-sided tape. All spectra were taken under a vacuum of about $10^{-8}$ Torr. Binding energies were calibrated to the symmetric C1s line (285.0 eV). No X-ray damage was observed.

### *Crystallography*

The X-ray measurements of **1** were carried out on a Philips PW-1100 single-crystal diffractometer (room temperature, Mo Kα radiation, $\lambda = 0.71069$ Å). Crystal and structure determination data are summarized in Table 1. Lp and in a later stage an empirical absorption [14] correction were applied. The position of Pt was obtained from a three-dimensional Patterson map. Subsequent $\Delta F$ syntheses provided the positions of the non-hydrogen atoms. Hydrogen atoms were ignored. All atoms were refined with anisotropic thermal parameters. Final atomic coordinates are given in Table 2. See also 'Supplementary Material'. The highest peak in the final difference map was 1.3 e $Å^{-3}$ (0.9 Å away from Pt1).

TABLE 1. Crystallographic data for *cis*-$(cpa)_2Pt(1\text{-}MeT)_2 \cdot 2H_2O$ (**1**)

| | |
|---|---|
| Formula weight | 623.6 |
| Space group | $P2_1/c$ |
| $a$ (Å) | 10.645(2) |
| $b$ (Å) | 14.878(3) |
| $c$ (Å) | 15.535(3) |
| $\beta$ (°) | 106.44(3) |
| $V$ ($Å^3$) | 2359.8 |
| $Z$ | 4 |
| $D_{calc}$ ($g\ cm^{-3}$) | 1.755 |
| Crystal size (mm) | 0.1, 0.1, 0.2 |
| $\mu$ ($cm^{-1}$) | 57 |
| $\theta$ range (°) | 2–25 |
| No. unique reflections | 3764 |
| No. reflections used in the calcltns. | 3758 $F_o > 2\sigma F_o$ |
| $R$ | 0.048 |
| $R_w(F)$ [a] | 0.054 |

[a] $w^{-1} = \sigma^2(F) + 0.0025F^2$.

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*Sample analyzed with Perkin-Elmer 240 elemental analyzer, Ar-purged (dehydrated) after weighing. Calculated value for H on assumption that weighted hydrate loses water completely.

TABLE 2. Atomic coordinates and equivalent isotropic temperature factors (Å$^2$) for **1**

| Atom | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Pt1 | 0.1473(1) | 0.4312(1) | 0.6159(1) | 0.028(1) |
| N10 | 0.0119(8) | 0.4616(5) | 0.6838(5) | 0.044(2) |
| C10 | 0.0323(14) | 0.4205(9) | 0.7721(8) | 0.076(5) |
| C11 | 0.1134(17) | 0.4746(17) | 0.8517(8) | 0.124(9) |
| C12 | −0.0331(17) | 0.4618(15) | 0.8365(9) | 0.113(8) |
| N20 | 0.0116(7) | 0.3540(5) | 0.5273(4) | 0.039(2) |
| C20 | −0.0164(10) | 0.2651(6) | 0.5628(7) | 0.049(3) |
| C21 | −0.1265(18) | 0.2525(10) | 0.5991(13) | 0.107(8) |
| C22 | −0.1344(16) | 0.2090(9) | 0.5093(9) | 0.091(6) |
| N1a | 0.3656(8) | 0.4589(6) | 0.4263(5) | 0.048(3) |
| C1a' | 0.3799(11) | 0.5307(8) | 0.3631(7) | 0.059(4) |
| C2a | 0.2855(8) | 0.4742(5) | 0.4824(5) | 0.033(2) |
| O2a' | 0.2287(7) | 0.5490(4) | 0.4812(4) | 0.047(2) |
| N3a | 0.2722(6) | 0.4068(4) | 0.5387(4) | 0.032(2) |
| C4a | 0.3220(9) | 0.3219(5) | 0.5350(5) | 0.037(2) |
| O4a' | 0.2998(7) | 0.2600(4) | 0.5799(4) | 0.049(2) |
| C5a | 0.4031(8) | 0.3109(5) | 0.4782(5) | 0.037(2) |
| C5a' | 0.4652(13) | 0.2209(7) | 0.4730(8) | 0.071(5) |
| C6a | 0.4210(10) | 0.3782(7) | 0.4255(6) | 0.048(3) |
| N1b | 0.3662(9) | 0.6577(5) | 0.7484(5) | 0.053(3) |
| C1b' | 0.3528(13) | 0.7571(6) | 0.7413(8) | 0.066(5) |
| C2b | 0.2613(9) | 0.6011(6) | 0.7003(5) | 0.040(3) |
| O2b' | 0.1588(7) | 0.6353(4) | 0.6570(5) | 0.056(2) |
| N3b | 0.2823(6) | 0.5097(4) | 0.7026(4) | 0.032(2) |
| C4b | 0.3879(8) | 0.4731(6) | 0.7627(5) | 0.038(2) |
| O4b' | 0.4015(6) | 0.3905(4) | 0.7713(4) | 0.053(2) |
| C5b | 0.4902(8) | 0.5320(6) | 0.8146(6) | 0.039(3) |
| C5b' | 0.6091(12) | 0.4900(9) | 0.8791(8) | 0.078(5) |
| C6b | 0.4788(9) | 0.6169(7) | 0.8059(6) | 0.051(3) |
| O10 | 0.2580(8) | 0.2656(5) | 0.2489(5) | 0.065(3) |
| O11 | 0.0908(10) | 0.1624(9) | 0.8374(9) | 0.137(6) |

Complex scattering factors for neutral atoms were taken from ref. 15. For calculations the SHELX program package was used [16].

## Results and Discussion

### *Crystal Structure of cis-(cpa)$_2$Pt(1-MeT)$_2$·2H$_2$O (1)*

Figure 1 shows the molecular structure of *cis*-(cpa)$_2$Pt(1-MeT)$_2$ (**1**) and gives the atom numbering scheme. Selected bond lengths and angles are listed in Table 3. Coordination of Pt is through the deprotonated N3 positions of the two 1-methylthymine rings, which are oriented head–head. This situation is special in that, with very few exceptions [17], two identical nucleobases in complexes of the type *cis*-[a$_2$ML$_2$]$^{n+}$ usually adopt a head–tail orientation (cf. also *cis*-(NH$_3$)$_2$Pt(1-MeU)$_2$ [18] and [(bpy)Au-(1-MeU)$_2$]$^+$ [19] and discussion in ref. 20). We are aware [21] that the pseudo-$C_2$ symmetry of the 1-MeT ligand does not permit a fully straightforward evaluation of the relative orientations of the two rings, but the somewhat differing electron densities of atoms N1 and C5 are in agreement with our description. Interestingly, the cyclopropyl groups of the cpa ligands are likewise on the same side of the Pt coordination plane. Because of the orientation of the two 1-MeT rings, **1** corresponds to a hypothetical cross-link of a *cis*-a$_2$Pt(II) entity with two thymine bases of DNA.

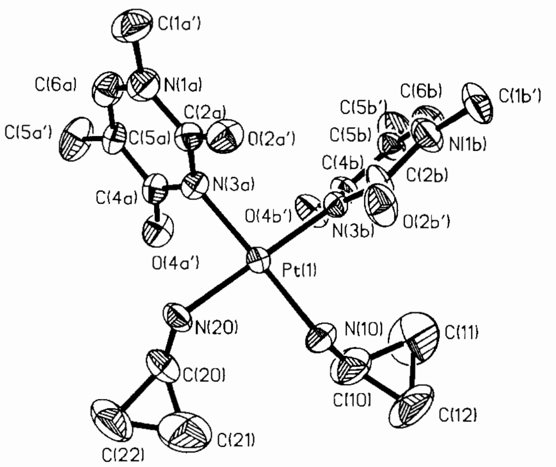

Fig. 1. Structure of *cis*-(cpa)$_2$Pt(1-MeT)$_2$ (**1**) showing the atom labeling scheme, 50% probability ellipsoids.

TABLE 3. Interatomic distances (Å) and angles (°) in **1**

| | | | |
|---|---|---|---|
| Pt1–N10 | 2.062(6) | C5a–C6a | 1.341(10) |
| Pt1–N20 | 2.044(5) | C6a–N1a | 1.339(10) |
| Pt1–N3a | 2.059(5) | N1b–C1b' | 1.486(10) |
| Pt1–N3b | 2.037(5) | N1b–C2b | 1.429(9) |
| N10–C10 | 1.462(11) | C2b–O2b' | 1.218(9) |
| C10–C11 | 1.523(17) | C2b–N3b | 1.378(9) |
| C10–C12 | 1.502(14) | N3b–C4b | 1.355(9) |
| C11–C12 | 1.521(18) | C4b–O4b' | 1.241(9) |
| N20–C20 | 1.495(9) | C4b–C5b | 1.451(9) |
| C20–C21 | 1.450(15) | C5b–C5b' | 1.510(11) |
| C20–C22 | 1.541(12) | C5b–C6b | 1.272(11) |
| C21–C22 | 1.518(17) | C6b–N1b | 1.413(10) |
| N1a–C1a' | 1.487(10) | | |
| N1a–C2a | 1.400(9) | | |
| C2a–O2a' | 1.265(8) | N10–Pt1–N20 | 90.3(2) |
| C2a–N3a | 1.364(8) | N10–Pt1–N3a | 175.0(2) |
| N3a–C4a | 1.377(8) | N10–Pt1–N3b | 90.0(2) |
| C4a–O4a' | 1.219(8) | N20–Pt1–N3a | 87.6(2) |
| C4a–C5a | 1.407(9) | N20–Pt1–N3b | 179.1(2) |
| C5a–C5a' | 1.506(10) | N3a–Pt1–N3b | 92.0(2) |

The geometries of the Pt coordination sphere, of the cpa ligands and of the 1-MeT rings are not unusual. In particular, structural parameters of the 1-MeT heterocycles agree well with those observed in *cis*-(NH$_3$)$_2$Pt(1-MeT)Cl, for example [22]. The planes (Table 4) of the two 1-MeT rings are close to planar as far as endocyclic ring atoms are concerned, although the N3 atoms deviate somewhat. At least

TABLE 4. Equation of planes, deviations of atoms and dihedral angles (°) between planes[a]

1. Pt-coordination plane

Equation: $-1.822x + 11.931y - 7.776z = 0.135$ Å

| N10* | N20* | N3a* | N3b* | Pt1 | C10 | C20 |
|---|---|---|---|---|---|---|
| 0.03 | −0.03 | 0.03 | −0.03 | −0.05 | −1.18 | −1.32 |

2. Cp-10 plane

Equation: $0.228x - 12.368y + 8.181z = 1.124$ Å

| C10* | C11* | C12* | Pt1 | N10 |
|---|---|---|---|---|
| 0.00 | 0.00 | 0.00 | −1.38 | −1.24 |

3. Cp-20 plane

Equation: $-3.274x + 12.296y - 5.674z = 0.120$ Å

| C20* | C21* | C22* | Pt1 | N20 |
|---|---|---|---|---|
| 0.00 | 0.00 | 0.00 | 1.21 | 1.20 |

4. 1-MeT-a plane

Equation: $6.684x + 4.414y + 7.960z = 7.864$ Å

| N1a* | C2a* | N3a* | C4a* | C5a* | C6a* |
|---|---|---|---|---|---|
| 0.00 | −0.02 | 0.04 | −0.03 | 0.01 | 0.01 |
| C1a′ | O2a′ | O4a′ | C5a′ | Pt1 | |
| −0.09 | −0.08 | −0.10 | −0.01 | −0.07 | |

5. 1-MeT-b plane

Equation: $-7.152x + 0.016y + 13.991z = 7.881$ Å

| N1b* | C2b* | N3b* | C4b* | C5b* | C6b* |
|---|---|---|---|---|---|
| −0.02 | 0.06 | −0.06 | 0.02 | 0.02 | −0.02 |
| C1b′ | O2b′ | O4b′ | C5b′ | Pt1 | |
| −0.02 | 0.19 | 0.05 | 0.07 | −0.31 | |

6. Angles between planes

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1–2 | 171.2 | 1–3 | 9.8 | 1–4 | 106.3 | | |
| 1–5 | 107.9 | 2–3 | 162.8 | 2–4 | 80.4 | | |
| 2–5 | 66.7 | 3–4 | 106.7 | 3–5 | 98.2 | | |
| 4–5 | 83.6 | | | | | | |

[a] Atoms with asterisks define the respective plane.

with the 1-MeT ring b, this may be related with the considerable deviation of Pt (0.31 Å) from the 1-MeT plane.

The dihedral angles, which were determined according to the convention introduced by Kistenmacher *et al.* [23], are 107.9° (ring b/Pt plane), 83.7° (ring a/Pt plane) and 83.6° (ring a/ring b). This angle between the two thymine rings is, albeit larger than in bis(guanine-N7) complexes [17], remarkably small considering other bis(pyrimidine) nucleobase complexes of *cis*-$a_2Pt(II)$ [24] or mixed pyrimidine, purine complexes [25].

The cyclopropyl triangles are almost parallel (Fig. 2) to the Pt coordination plane (dihedral angles 9° av.) and form a small angle of 17.2° with respect to each other.

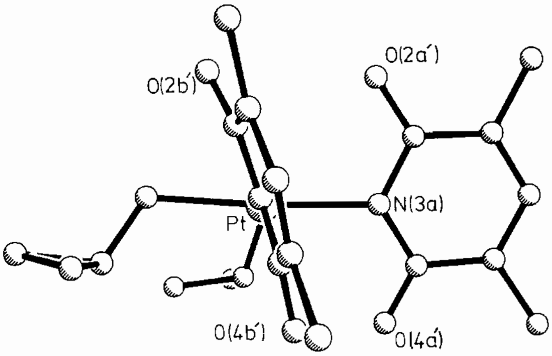

Fig. 2. Base/base dihedral angle between 1-MeT planes in 1 as determined according to ref. 23.

TABLE 5. Hydrogen bonds in 1: distances (Å), angles (°)

| | | | |
|---|---|---|---|
| N10–O2a′[1] | 3.07(1) | Pt1–N10–O2a′[1] | 95.8(3) |
| N20–O2a′[1] | 2.91(1) | Pt1–N20–O2a′[1] | 101.3(3) |
| N20–O2b′[1] | 2.93(1) | Pt1–N20–O2b′[1] | 138.8(4) |
| N20–O11[2] | 3.30(2) | Pt1–N20–O11[2] | 109.4(4) |
| O10–O11[2] | 2.75(2) | | |
| O4a′–O10[3] | 2.81(1) | C4a–O4a′–O10[3] | 138.2(6) |
| O4b′–O10[3] | 2.75(1) | C4b–O4b′–O10[3] | 141.3(6) |
| N10–O11[4] | 3.17(2) | Pt1–N10–O11[4] | 115.1(4) |
| O2b′–O11[4] | 2.71(2) | C2b–O2b′–O11[4] | 140.9(8) |

Symmetry operations: [1] $-x, 1-y, 1-z$; [2] $x, 0.5-y, -0.5+z$; [3] $x, 0.5-y, 0.5+z$; [4] $-x, 0.5+y, 1.5-z$.

In the crystal, intermolecular hydrogen bonding is observed between the amine nitrogens of the cpa rings and O2 sites and water molecules, between O2 and water molecules, between O4 and water, and between two water molecules. Distances are in the range of 2.71–3.30 Å (Table 5).

### *$^1$H NMR Spectra of 1*

$^1$H NMR resonances of 1 in $D_2O$ (pD = 3.8) are observed at 7.22 (H6), 3.28 ($N{-}CH_3$) and 1.77 ($C{-}CH_3$) ppm. All resonances are shifted upfield relative to those of neutral 1-methylthymine similar to the bis(1-methylthyminato) complexes of *cis*-$(NH_3)_2Pt(II)$ [12]. Resonances of the amine ligand are observed at 2.48 ppm (an ill-resolved multiplet of C–H) and between 0.64 and 0.55 ppm ($-CH_2-$).

There is no indication of additional signal splitting at 20 °C that could be attributed to the existence of stable rotamers with a high barrier of rotation as observed with the bpy containing bis(thyminato) complexes of Pd(II) and Pt(II) and the bis(uracilato) complex of Au(III) [19].

### *Protonation of 1*

Protonation of 1 with $DNO_3$ was followed by $^1$H NMR spectroscopy. Resonances of the 1-MeT ligands, which have essentially constant shifts in the pD range 12–4, undergo downfield shifts at lower pH. In the case of the H6 resonance, the downfield shift is sigmoidal in the range $0.4 \leqslant pH^* \leqslant 4$, with a $\delta$ of 0.4 ppm and a $pK_a$ of 3.0. The magnitude of the downfield shift [26] suggests a single protonation step, hence the presence of *cis*-$[(cpa)_2Pt(1\text{-MeT})(1\text{-MeTH})]^+$ at pH* 0.4–1. No indication of a second protonation step leading eventually to *cis*-$[(cpa)_2Pt(1\text{-MeTH})_2]^{2+}$ is to be seen at pH* 0.4. The $pK_a$ of 3.0 is markedly different from related *cis*-$[(NH_3)_2PtL(LH)]^+$ species with L = 1-MeT (2.0), 1-MeU (1.4) etc. [27].

**1** is unstable in acidic medium. Below pD 1, the formation of free 1-MeTH (H6, 7.46 ppm) besides protonated **1** (H6, 7.57 ppm), protonated cpa and transient *cis*-$[(cpa)_2Pt(1\text{-MeT})_2Pt(cpa)_2]^{2+}$ (H6, 7.35 ppm) is observed, very similar to *cis*-$(NH_3)_2Pt(1\text{-MeU})_2$ [18]. The $^1H$ NMR spectra of such a sample shows after a few days and subsequent heating, the resonances of free 1-MeTH only. Liberation of cpa is observed even at pD 3.5 and recognized not only in the $^1H$ NMR spectrum (Fig. 3) but also from the rise in pD. The identity of the resonances due to cpa/cpaH$^+$ has been unambiguously established by variable pH measurements (see below).

Protonation of **1** in all cases is accompanied by formation of a pink and purple species, respectively, with a $\lambda_{max} = 550$ nm, depending on the treatment of the sample. For example, warming to 60 °C (30 min) gives an intensely purple solution from which a material with features (IR, UV–Vis, elemental analysis) similar to those of the 1-MeT purple prepared according to Thomson *et al.* [8] was isolated also only in low yield.

*Reactivity of 1 towards Metals*

Like other $a_2PtL_2$ complexes (a = $NH_3$, L = 1-MeT or 1-MeU) [1, 28], **1** readily binds additional metal electrophiles. For example, a yellow color develops instantaneously when $Cu^{2+}$ is added to an aqueous solution of **1**, very much as with *cis*-$(NH_3)_2Pt(1\text{-MeT})_2$ [29]. With *cis*-$[(NH_3)_2Pt(H_2O)_2]^{2+}$ and *cis*-$[(cpa)_2Pt(H_2O)_2]^{2+}$ respectively, dinuclear compounds of composition *cis*-$[(cpa)_2Pt(1\text{-MeT})_2Pta_2]^{2+}$ (a = $NH_3$ (**2**) or cpa (**3**)) form and $K_2PtCl_4$ reacts with **1** to give *cis*-$(cpa)_2Pt(1\text{-MeT})_2PtCl_2$ (**4**). These reactions also take place with *cis*-$(NH_3)_2Pt(1\text{-MeT})_2$ [13, 21], but yields are much smaller in the case of **1**. Moreover, reaction of **1** with $[a_2Pt(H_2O)_2]^{2+}$ (a = $NH_3$ or cpa) always leads to an intensely purple byproduct which, according to its main absorption ($\lambda_{max} = 550$ nm) is similar or identical with the 'purple' described by Thomson *et al.*

The $^1H$ NMR spectrum of **2** shows downfield shifts of 1-MeT resonances, characteristic of N3, O4 bridged complexes. H6 resonances are at 7.27 ppm, the resonances of N–$CH_3$ and C–$CH_3$ at 3.34 and 1.81 ppm.

The IR spectra also show the typical modes for a N3, O4 coordination, viz. a splitting in the double bond stretching region in three intensive modes at 1660, 1575 and 1515 cm$^{-1}$.

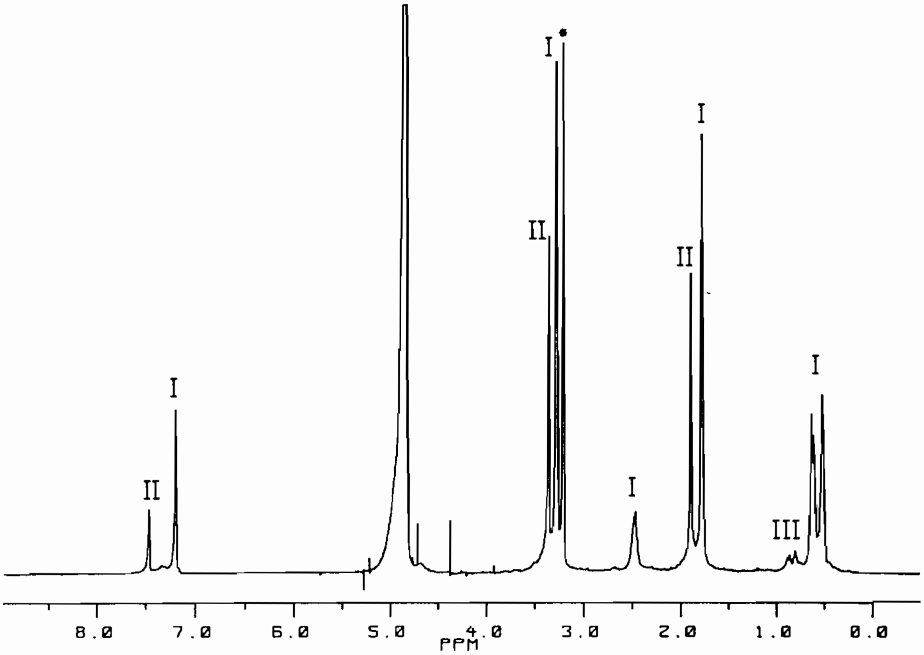

Fig. 3. $^1H$ NMR spectra (300 MHz) of **1** after acidification with $DNO_3$ and after 10 d; (pD 6.3) * = $N(Me_4)_4^+$, I = **1**, II = 1-MeTH, III = cpaH$^+$.

Compounds 3 could not be obtained in a pure form. The isolated precipitates always contain an excess of $NaNO_3$ or $NaClO_4$. However, $^1H$ NMR spectra and IR spectra, and, in the case of the $ClO_4^-$ product, the C:N ratio of elemental analysis leave no doubt that these compounds are N3, O4 bridged diplatinum complexes. H6 resonances of 3 are at 7.34 ppm, the N–$CH_3$ and C–$CH_3$ resonances at 3.36 and 1.86 ppm respectively. Resonances of 2 are thus between those of 3 and the $[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2]^{2+}$ complex (7.27, 3.34 and 1.81 ppm) as expected. Because of poor solubility of 4 in all common solvents, $^1H$ NMR spectra could not be obtained. However, the IR spectra of 4 show the typical modes of N3,O4 bridged complexes with three characteristic bands at 1660, 1580 and 1515 $cm^{-1}$ and in addition the Pt–Cl stretching mode at 335 $cm^{-1}$.

*Solution Behavior of cis-(cpa)$_2$PtCl$_2$*

As outlined above, cpa is lost from *cis*-$(cpa)_2Pt(1\text{-}MeT)_2$ in moderately and strongly acidic medium. We also found that under conditions close to those applied by Thomson *et al.* during the preparation of the 'purple', *cis*-$(cpa)_2PtCl_2$ loses cpa. Figure 4(a) shows the $^1H$ NMR spectrum of *cis*-$(cpa)_2PtCl_2$ in $D_2O$, pD 4.9, recorded immediately after sample preparation (I). After 3 h, the spectrum displays an additional set (II) of $^1H$ resonances assigned to the aliphatic protons of *cis*-$[(cpa)_2Pt(H_2O)_2]^{2+}$ from comparison with a sample prepared from the dichloro species and $AgNO_3$ (Fig. 4(b)). After three days a third set of $^1H$ resonances (Fig. 4(c), III) is present, which intensifies greatly when the sample is kept at 70 °C for 30 min. From pD dependent spectra as well as from comparison with free cpa, the new resonances III can unambiguously be identified as being due to cpa/cpaH. Prolonged heating (80 °C) eventually leads to complete decomposition and formation of Pt(0) as identified by elemental analysis.

It seems likely that protonation of the cpa ligand after liberation from the complex is an important requisite to prevent reformation of the Pt–cpa bond [30]. The protons to accomplish this must be from acidic solvolysis products of *cis*-$(cpa)_2PtCl_2$. A possible sequence could involve

$$(cpa)_2PtCl_2 + H_2O \longrightarrow (cpa)_2PtCl(OH) + H^+$$

$$\Big\downarrow H_2O$$

$$(cpa)(H_2O)PtCl(OH) + cpaH^+$$

*Oxidation of 2 and 3*

In weakly acidic solution, 2 is readily oxidized by $Ce^{4+}$, primarily to a product having a characteristic absorption at 740 nm. Although we have not attempted to isolate the product formed, we are convinced that it is the analogue of the 'Pt(2.25)–1-MeU-blue', which absorbs at the very same wavelength. Formation of a tetranuclear compound certainly is possible on steric grounds in that the $(NH_3)_2Pt(O4)_2$ entities facing each other, are identical in both cases.

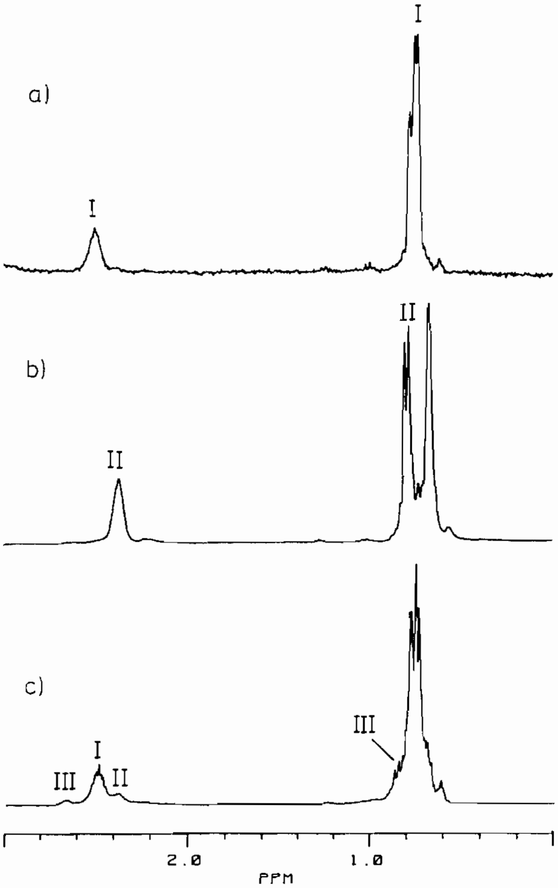

Fig. 4. $^1H$ NMR spectra (300 MHz) of (a) *cis*-$(cpa)_2PtCl_2$ immediately after sample preparation (pD = 4.9); (b) *cis*-$[(cpa)_2Pt(H_2O)_2](NO_3)_2$ (pD = 2.6); (c) *cis*-$(cpa)_2PtCl_2$ after 3 days and heating (70 °C, 30 min) (pD = 4.6). I, II, III refer to *cis*-$(cpa)_2PtCl_2$, *cis*-$[(cpa)_2Pt(H_2O)_2]^{2+}$ and $cpaH^+$.

In contrast, oxidation of 3 with $HClO_4$ and $HNO_3$ does not produce an analogue of the former but rather gives a 'purple' absorbing again at 550 nm.

In the case of oxidation with $HClO_4$, a very small amount of a purple precipitate could be isolated. The IR spectrum reveals no similarity with that of a $[Pt(2.0)]_2$ compound as would be expected for a $[Pt(2.25)]_4$ complex. Rather, this compound shows a close similarity with the IR spectrum of the 'purple', isolated by Thomson *et al.*, if one ignores the intense bands of $ClO_4^-$.

It seems obvious that the relatively bulky cpa ligands prevent any close approach of the two $Pt_2$ entities that might enable metal–metal bond formation during oxidation, so that there must be an alternative way for building up a mixed-valence compound.

Thomson *et al.* prepared their 'purple' by reacting *cis*-(cpa)$_2$PtCl$_2$ with 1-MeTH for 1 h at 60 °C, followed by two consecutive precipitations from $H_2O$ (as B(Ph)$_4$ salt) and from acetone (as Cl salt). Their formulation of the 'purple' as $Pt_6(1\text{-MeT})_4(cpa)_6(OH)_{10}Cl_8$ was based, among others, on elemental analysis data and oxidation titration with Ce(IV), believed to proceed to the Pt(IV) state. The authors' statement that amine ligands have been displaced from the Pt metal center during reaction with 1-MeT is supported by our findings. A liberation of cpa is observed both preparing the 'purple' from *cis*-(cpa)$_2$PtCl$_2$ or **1**.

On the other hand, we disagree with the authors' suggestion on the metal oxidation state. ESCA has been shown to be a useful method for determining the oxidation state of platinum compounds from Pt4f binding energies. Pt(II) complexes have Pt4f$_{7/2}$ binding energies between 72.4 and 74.3 eV, Pt(IV) complexes between 75.5 and 76.8 [31] and the few characterized Pt(III) complexes are about 75 eV [32]. Our B(Ph)$_4$ salt of the 'purple' has a Pt4f$_{7/2}$ binding energy of 73.6 eV (Pt4f$_{5/2}$ 76.6 ± 0.2 eV, not well resolved), quite similar to the values of other platinum blues (α-pyridone-, uracil-, acetamide-blue [33]). There is also no evidence for different sets of Pt4f binding energies which points toward a valence delocalized system.

ESCA data therefore suggest that the average Pt oxidation state in fact is close to +2 rather than +3.72 as proposed. Moreover, at the time of Thomson's study, the existence of stable diplatinum(III) oxidation products was yet unestablished [34]. Consequently, Ce(IV) oxidation may have produced dinuclear Pt(III) rather than the anticipated mononuclear Pt(IV) compounds. Finally, we note that scanning electron microscopy occasionally revealed the presence of potassium (from starting material *cis*-(cpa)$_2$PtCl$_2$ ?) in the B(Ph)$_4$ salt of the 'purple' and FAB-MS proved LiCl to be present in the acetone precipitate.

Our present data do not provide conclusive evidence concerning the proper formulation of the 'purple'. We can exclude, however, a dimer-of-dimer structure analogous to [Pt(2.25)]$_4$, although the established loss of cpa ligands would, in principle, permit the close approach of two dinuclear units. From our ongoing studies with mixed-valence complexes in the *cis*-(NH$_3$)$_2$Pt/1-MeT(1-MeU)/Cl$^-$ system we now have results supported by X-ray analysis [35] that dinuclear, μ-Cl bridged entities do exist and that they absorb in a spectral region very close to that of the 'purple' discussed here [7]. The presence of Cl$^-$ in B(Ph)$_4$ salts of the 'purple', as demonstrated by scanning electron microscopy, would certainly fit into this picture.

## Supplementary Material

Positional parameters and anisotropic temperature factors of **1**, short contacts and a listing of observed and calculated structure factors can be obtained from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2 under CSD 53878 on request. Requests should be accompanied by the complete literature citation.

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## Note Added in Proof

Since this manuscript was completed, an octanuclear Pt acetamide complex with a Pt(2.25) average oxidation state has been reported: K. Sakai and K. Matsumoto, *J. Am. Chem. Soc., 111* (1989) 3074. Based on the intramolecular Pt...Pt separations within the four dinuclear cations, this compound might be considered an adduct of a tetranuclear Pt(2.5) entity with two dinuclear Pt(2.0) entities.