A novel binding mode of the N(6)-deprotonated adenine. Synthesis, spectroscopic characterization and X-ray structure of bis(μ-9-ethyladeninato-N^1,N^6) bis(bis(trimethylphosphine)platinum(II) dinitrate

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Abstract

9-Ethyladenine (9-EtAd) reacts with *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ in aqueous solution at ambient temperature to give the adduct *cis*-$[(PMe_3)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2(NO_3)_2$ which has been characterized in the solid state by single-crystal X-ray analysis. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 10.359(5)$, $b = 11.224(5)$, $c = 21.056(9)$ Å, $\alpha = 85.09(3)$, $\beta = 88.69(4)$, $\gamma = 83.90(4)°$, $Z = 2$. The structure was solved from 3455 reflections to $R = 0.075$. The molecular structure of the cationic complex exhibits two *cis*-$(PMe_3)_2Pt$ units which are bridged by two NH_2-deprotonated adenine molecules through the N(1) and N(6) atoms (mean Pt–N distance of 2.10 Å) in a head-to-tail fashion. The two purine rings are virtually perpendicular (dihedral angle of 101.4°) and each ring forms with the platinum coordination planes angles of 87.6 and 89.3°. The complex has been characterized in solution by ^1H and ^{31}P NMR spectroscopy. The H(2) and H(8) resonances, which are indistinguishable in the proton spectrum of the free base, appear well differentiated upon platination of the nucleobase, with the H(2) proton coupled to the metal centre (^3J(PtH) 15.5 Hz). The presence of long-range platinum–phosphorus interactions in the ^{31}P spectrum indicates that the dinuclear structure found in the solid state is maintained in solution.

Introduction

Platinum(II) complexes with 9-alkylsubstituted adenines are well known [1]. In most of them the nucleobase is bonded to the metal centre in a unidentate fashion, generally through the N(7) or, more rarely, through the N(1) atom. The simultaneous coordination of the nucleobase at two metal centres, through the N(7) and N(1) atoms, has also been established in dinuclear [2] and trinuclear [3] platinum(II) derivatives of 9-methyladenine (9-MeAd). On the contrary, complexes containing N(6)-deprotonated adenine ligands are rare. To our knowledge, the only structurally characterized example appears to be the mononuclear complex $[Cp_2Mo(9\text{-}MeAd(-H))]^+$ ($Cp = \eta^5\text{-}C_5H_5$) in which the nucleobase forms a four-membered chelate ring [4].

In the frame of our ongoing interest on the interaction of nucleobases and nucleosides with trimethylphosphine complexes of platinum(II) [5], we have investigated the reaction of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ with 9-ethyladenine (9-EtAd). In this paper we describe the synthesis and the complete characterization of the dinuclear complex *cis*-$[(PMe_3)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2(NO_3)_2$ in which the N(6)-deprotonated nucleobase exhibits an unprecedented binding mode.

Experimental

Preparation of cis-$[(PMe_3)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2(NO_3)_2$

73.8 mg (0.452 mmol) of 9-EtAd (from Sigma) were added to a solution of *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ [5a] (193 mg, 0.226 mmol) in H_2O (15 ml) and the resulting solution was stirred at room temperature for 48 h. The solvent was then vacuum evaporated and the residue was dissolved in a mixture of EtOH (2 ml)/MeOH (2.5 ml). Addition of Et_2O afforded a white precipitate which was isolated by filtration and dried under vacuum. The yield was 219 mg, 85%. *Anal.* Calc. for $C_{13}H_{26}N_6O_3P_2Pt$: C, 27.32; H, 4.58; N, 14.71. Found: C, 26.9; H, 4.7; N, 14.9%. ^1H NMR in DMSO-d_6, at

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27 °C: (adenine resonances) 8.12 (singlet, 1H, H(8)), 8.09 (singlet with ^{195}Pt satellites, ^{3}J(H–Pt) 15.5 Hz, 1H, H(2)), 6.60 (broad s, 1H, NH), 4.03 (quartet, J(H–H) 7.3 Hz, 2H, CH$_2$), 1.30 (t, J(H–H) 7.3 Hz, 3H, CH$_3$); (PMe$_3$ resonances) 1.87 (d, ^{2}J(H–P) 11.1 Hz, ^{3}J(H–Pt) 34.6 Hz, 9H), 1.43 (d, ^{2}J(H–P) 10.5 Hz, ^{3}J(H–Pt) 32.8 Hz, 9H). ^{31}P{^{1}H} NMR in D$_2$O, at 27 °C: −31.02 (^{2}J(PP) 25.6 Hz, ^{1}J(PtP) 3026 Hz), −31.59 (^{2}J(PP) 25.6 Hz, ^{1}J(PtP) 3198 Hz).

X-ray crystallography

Crystals in the form of regularly shaped colorless parallelepipeds, suitable for X-ray analysis, were obtained by condensing vapours of Et$_2$O into an alcoholic solution of the complex, at room temperature, for several days. The crystals were found to be very unstable in the absence of their mother liquor and they opacized rapidly when removed from the solution. A crystal was therefore directly inserted in a Lindeman capillary previously fitted with a drop of mother solution. The capillary was then sealed using an electrically heated platinum wire. Crystal data are listed in Table 1.

Data were collected on a Siemens Nicolet R3m/V four-circle diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The scan width was 1.36° and the scan speed varied from 6.51 to 14.65° min^{-1}. Of a total of 4466 unique data collected in the range 2ϑ 4.5–40°, only 3455 with $|F_o| > 4\sigma(|F_o|)$ were used in subsequent stages. The upper limit of 2ϑ was limited to 40° since at higher values a drastic decrease of the diffraction power was preliminary observed. The high value 4σ is due to the need to carry out the data collection with an adequate high speed, because the crystal in time undergoes decomposition. In fact, the intensity decay of two standard reflections monitored at 1 h intervals was up to 30% and decay correction was applied to the data. No absorption corrections were applied, because the effects due to absorption and/or decay were not distinguishable.

TABLE 1. Crystal data for *cis*-[(PMe$_3$)$_2$Pt(μ-9-EtAd($-$H))]$_2$(NO$_3$)$_2$

Formula weight	1142.9
Crystal size (mm)	0.2×0.3×0.4
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	10.359(5)
b (Å)	11.224(5)
c (Å)	21.056(9)
α (°)	85.09(3)
β (°)	88.69(4)
γ (°)	83.90(4)
V (Å^3)	2423(4)
Z	2
D_{calc} (g cm^{-3})	1.57
μ (mm^{-1})	5.9
No. unique reflections	4466
No. observed reflections	3455
No. parameters	275
R	0.075
$R_w(F)$	0.080

Structure solution and refinement

The Pt and P atoms were located from a Patterson synthesis; the remaining non-hydrogen atoms were found from successive difference syntheses. The Pt, P and ten N atoms of the two adeninate ligands were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement, in which the quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized, with $w = \sigma^2(F_o) + 0.0347(F_o)^2$. The final R and R_w were 0.075 and 0.080, respectively, with goodness-of-fit equal to 0.55*. In the final ΔF maps the C(11) atom of an ethyl group assumed two orientations with occupancy factor of *c.* 0.50. No relevant peaks were observed in the final ΔF map, apart from two peaks of height *c.* 1.2 e Å^{-3} at 1.1 Å from the Pt atoms and the packing diagrams did not exhibit any cavity where liquor mother molecules could arrange. Neutral atom scattering factors and corrections for anomalous dispersion were taken from the usual source [6] and the programs package system was SHELXTL-PLUS [7]. Fractional atomic coordinates are listed in Table 2, while Table 3 lists the bond lengths and angles relative to the 'inner core' of the complex.

Results and discussion

When a stoichiometric amount of 9-EtAd is added to a solution of *cis*-[(PMe$_3$)$_2$Pt(μ-OH)]$_2$(NO$_3$)$_2$ in aqueous solution at room temperature, the following reaction occurs in a few hours:

$$cis\text{-}[(\mathrm{PMe_3})_2\mathrm{Pt}(\mu\text{-OH})]_2{}^{2+} + 2\ \text{9-EtAd} \longrightarrow$$
$$cis\text{-}[(\mathrm{PMe_3})_2\mathrm{Pt}(\mu\text{-9-EtAd}(-\mathrm{H}))]_2{}^{2+} + 2\mathrm{H_2O}$$

The reaction product was characterized in the solid state by single crystal X-ray analysis and in solution by ^{1}H and ^{31}P NMR spectroscopy.

Figure 1 illustrates the molecular geometry and the labelling scheme for the cation [(PMe$_3$)$_2$Pt(μ-9-EtAd($-$H))]$_2{}^{2+}$, while Table 3 lists selected bond lengths and angles. As can be seen from the e.s.d.s, the structure is not a particularly accurate one (see 'Experimental'), but it does answer a chemical question and the model provides an adequate conclusion about binding/stereochemistry features. The complex contains a dimeric cation in which two square-planar arrays around each platinum atom are bridged in the *cis* positions by the adeninate ligand through the N(1)

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*GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_v)]^{1/2}$.

TABLE 2. Atomic coordinates and equivalent isotropic displacement coefficients[a]

	x	y	z	U
Pt	0.0355(1)	0.2236(1)	0.1925(1)	0.029
Pt'	0.1995(1)	0.4428(1)	0.2131(1)	0.030
P(1)	0.1045(5)	0.1399(5)	0.1026(3)	0.036
P(2)	0.1040(6)	0.0559(5)	0.2569(3)	0.041
P(1')	0.4005(5)	0.3713(5)	0.2467(3)	0.040
P(2')	0.2708(5)	0.5282(5)	0.1196(3)	0.038
O(1)	0.744(2)	0.129(2)	0.010(1)	0.102
O(2)	0.730(2)	0.212(2)	0.093(1)	0.134
O(3)	0.565(3)	0.210(2)	0.032(1)	0.138
O(1')	0.749(3)	0.424(3)	0.618(1)	0.146
O(2')	0.795(4)	0.222(4)	0.630(2)	0.234
O(3')	0.720(3)	0.335(3)	0.710(2)	0.163
N(1)	−0.053(1)	0.298(1)	0.2740(7)	0.033
N(3)	−0.242(2)	0.279(2)	0.3397(9)	0.058
N(6)	0.126(1)	0.399(1)	0.3018(8)	0.039
N(7)	−0.019(2)	0.420(2)	0.4293(9)	0.070
N(9)	−0.218(2)	0.361(2)	0.4427(9)	0.076
N(18)	0.680(2)	0.183(2)	0.043(1)	0.067
N(1')	0.010(1)	0.528(1)	0.1893(7)	0.029
N(3')	−0.099(1)	0.731(1)	0.1801(9)	0.045
N(6')	−0.066(1)	0.374(1)	0.1413(7)	0.037
N(7')	−0.275(1)	0.558(1)	0.0871(7)	0.037
N(9')	−0.276(2)	0.750(1)	0.1116(9)	0.050
N(18')	0.768(3)	0.322(3)	0.654(2)	0.105
C(2)	−0.170(2)	0.263(2)	0.287(1)	0.047
C(4)	−0.174(2)	0.333(2)	0.383(1)	0.049
C(5)	−0.056(2)	0.369(2)	0.376(1)	0.049
C(6)	0.011(2)	0.360(2)	0.317(1)	0.045
C(8)	−0.113(3)	0.408(2)	0.469(1)	0.080
C(10)	−0.331(3)	0.319(3)	0.479(2)	0.099
C(11)[b]	−0.416(9)	0.426(8)	0.480(4)	0.174
C(11a)[b]	−0.320(9)	0.199(8)	0.497(4)	0.141
C(12)	0.280(2)	0.107(2)	0.089(1)	0.055
C(13)	0.035(2)	−0.002(2)	0.093(1)	0.059
C(14)	0.053(2)	0.229(2)	0.029(1)	0.058
C(15)	0.149(3)	0.087(2)	0.339(1)	0.074
C(16)	0.240(3)	−0.044(2)	0.235(1)	0.081
C(17)	−0.032(2)	−0.037(2)	0.271(1)	0.073
C(2')	−0.005(2)	0.640(2)	0.203(1)	0.042
C(4')	−0.175(2)	0.684(2)	0.1420(9)	0.033
C(5')	−0.174(2)	0.571(1)	0.1276(8)	0.024
C(6')	−0.079(2)	0.482(1)	0.1520(9)	0.028
C(8')	−0.335(2)	0.668(2)	0.077(1)	0.061
C(10')	−0.314(2)	0.875(2)	0.111(1)	0.067
C(11')	−0.394(5)	0.920(5)	0.167(2)	0.183
C(12')	0.407(2)	0.328(2)	0.330(1)	0.073
C(13')	0.526(3)	0.474(2)	0.232(1)	0.067
C(14')	0.469(2)	0.231(2)	0.214(1)	0.063
C(15')	0.316(2)	0.682(2)	0.132(1)	0.068
C(16')	0.400(2)	0.454(2)	0.075(1)	0.049
C(17')	0.150(2)	0.566(2)	0.060(1)	0.066

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Occupancy factor: 0.5.

TABLE 3. Selected bond lengths (Å) and angles (°) for *cis*-$[(PMe_3)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2(NO_3)_2$

Pt–P(1)	2.253(5)	P(1)–Pt–P(2)	93.6(2)
Pt–P(2)	2.283(5)	P(1)–Pt–N(1)	172.9(4)
Pt'–P(1')	2.257(5)	P(2)–Pt–N(1)	87.9(4)
Pt'–P(2')	2.257(5)	P(1)–Pt–N(6')	92.7(4)
Pt–N(1)	2.12(1)	P(2)–Pt–N(6')	168.1(4)
Pt–N(6')	2.11(1)	N(1)–Pt–N(6')	84.7(6)
Pt'–N(6)	2.04(2)	P(1')–Pt'–P(2')	94.1(2)
Pt'–N(1')	2.14(1)	P(1')–Pt'–N(6)	89.9(4)
P–C(mean)	1.83(2)	P(2')–Pt'–N(6)	168.9(4)
		P(1')–Pt'–N(1')	172.8(4)
		P(2')–Pt'–N(1')	87.6(4)
		N(6')–Pt'–N(1')	87.2(6)

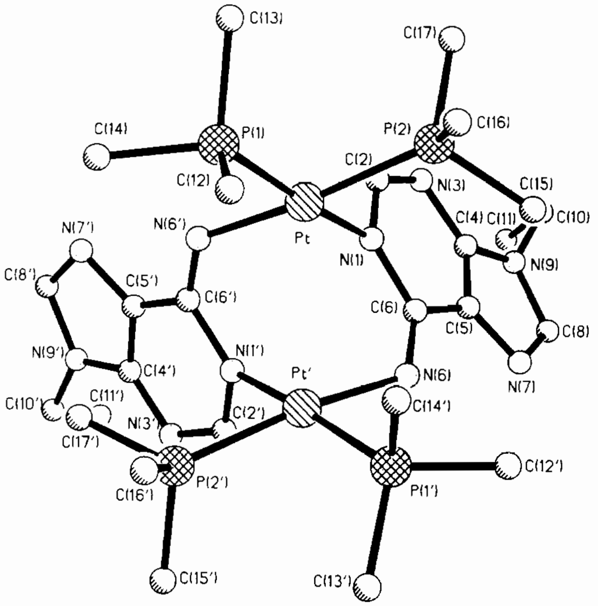

Fig. 1. Diagram of the cation $[(Me_3P)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2^{2+}$ with the platinum atoms in the plane of the paper. Nitrate groups are omitted for clarity.

atom and the deprotonated exocyclic amine group N(6) atom. Each Pt atom has a P_2N_2 square-planar (within 0.03(1) Å) coordination and deviates significantly (0.16 Å) from the mean plane of the four donors. The N(1)---N(6') and N(1')---N(6) bite distances (2.85 and 2.88 Å, respectively) are considerably shorter than the Pt---Pt' separation (3.20 Å) and this difference causes the formation of a dihedral angle of 48.6° between the coordination planes of the two metal centres. In addition, the two square planar units are rotated by *c.* 25°, so that the atoms coordinated to one platinum atom do not lie directly above those coordinated to other one as can be seen in Fig. 2, in which the cation is viewed down the Pt–Pt' vector.

This unprecedented bonding mode of the nucleobase closely parallels that found in *cis*-$[(Me_3P)_2Pt(\mu\text{-}1\text{-}MeCy(-H))]_2(NO_3)_2$ [5a], in which two 1-methyl substituted cytosine anions (1-MeCy(− H)) bridge two metal centres through the N(3), N(4) atoms, in a head-to-tail fashion. The two ten-membered adeninate ligands are roughly planar (maximum deviation of 0.05 Å) and

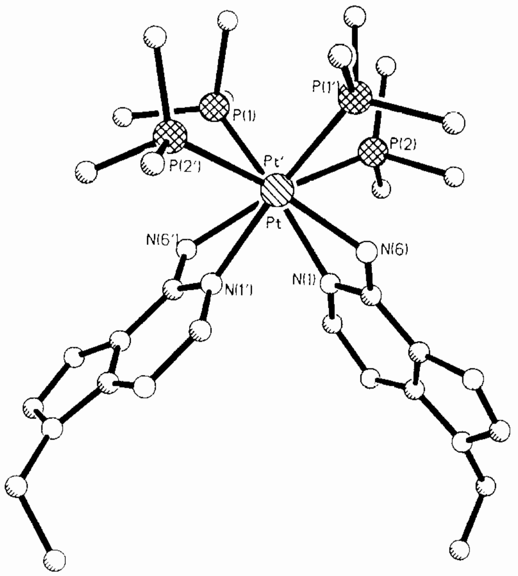

Fig. 2. The cation $[(Me_3P)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2^{2+}$ viewed down the Pt–Pt' vector, showing the twist of the two square planes.

virtually perpendicular each other (dihedral angle of 101°). Each ring forms with the platinum coordination planes angles of 87.6 and 89.3°. The platinum–phosphorus bond lengths and angles within the *cis*-$(Me_3P)_2Pt$ units show no significant differences from those of related complexes [5].

The crystal structure consists of the cation and two nitrate anions disposed in general positions within the unit cell. The atoms of the NO_3^- exhibit large, but not unusual, thermal parameters and their interactions fall within the range of distances observed for other Pt(II)–nucleobase complexes [5]. In particular, the intermolecular contacts N(6')---O(2) (at $1+x$, y, z) and N(6)---O(1') (at $1-x$, $1-y$, $1-z$) (3.17 and 3.11 Å, respectively) represent the only possible, but very weak, hydrogen bonds, while the remaining interactions, including the Pt'---O(3') (at $1-x$, $1-y$, $1-z$) separation of 3.28 Å, are at or greater than van der Waals contact distances.

The complex has been also characterized by ^1H and ^{31}P NMR spectroscopy. The main feature of the proton spectrum is related to the adenine H(2) and H(8) resonances which appear resolved (at δ 8.09 and 8.12, respectively, in DMSO-d_6) whereas they occur as a single resonance, centred at 8.15 ppm (at 89.55 MHz), in the free base. The higher field singlet, flanked by ^{195}Pt satellites (^3J(PtH) 15.5 Hz) is attributable to the H(2) proton. The N(6)H resonance is observed as a broad singlet centred at 6.60 ppm, shifted 0.56 ppm upfield with respect to the uncoordinated base. As expected, this resonance is not detectable in D_2O owing to the chemical exchange of the NH proton with the solvent. Moreover, in this latter solvent the H(2) and H(8) resonances occur in the opposite order, being centred at δ 8.20 (^3J(PtH) 16.2 Hz) and 7.96 ppm, respectively. The fact that only one of the purine ring protons exhibits ^{195}Pt satellites indicates that the N(1) and N(7) binding sites do not compete in the coordination to the metal [8]. This conclusion is supported by the ^{31}P NMR data obtained in D_2O and DMSO-d_6.

In line with the proton spectrum, which exhibits two sets of resonances for the phosphine methyl protons (see 'Experimental'), the corresponding ^{31}P NMR spectrum shows a second order multiplet, flanked by ^{195}Pt satellites, centred at −30.38 (^1J(PtP) 3000 Hz) and −31.01 (^1J(PtP) 3237 Hz) ppm, respectively, in agreement with the presence of two chemically unequivalent PMe_3 ligands in mutual *cis* position (^2J(PP)26.2 Hz).

As shown in Fig. 3, the AB multiplet is symmetrically flanked by additional weak resonances attributable to long-range ^{195}Pt–^{31}P coupling effects. A very similar pattern is found in D_2O solution, with only minor changes of the chemical shift and coupling constant values (see 'Experimental').

In the structurally related complex, *cis*-$[(Me_3P)_2Pt(\mu\text{-}1\text{-}MeCy(-H))]_2^{2+}$, in which the phosphine ligands are *trans* to the N(3) and N(4) atoms of the deprotonated 1-methylcytosine, the ^{31}P pattern is centred at δ −31.91 (^1J(PtP) 3066 Hz, ^2J(PP) 26.2 Hz) and −32.44 (^1J(PtP) 3269, ^2J(PP) 26.2 Hz) in DMSO-d_6 and at δ −32.75(^1J(PtP) 3135, ^2J(PP) 26.2 Hz) and −33.03 (^1J(PtP) 3293, ^2J(PP) 26.2 Hz) ppm in D_2O, respectively [5a]. Moreover, the main resonances are flanked by weak satellites, due to long-range ^{195}Pt–^{31}P interactions, whose positions and intensities are very similar to those found in the spectrum of *cis*-$[(PMe_3)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2^{2+}$. The strict similarity of the ^{31}P NMR data obtained for the cytosine and adenine complexes rules out the involvement of the N(7) as donor site towards the metal centre in the solutions of *cis*-$[(PMe_3)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2^{2+}$.

Fig. 3. $^{31}P\{^1H\}$ NMR spectrum (at 36.23 MHz) of $[(Me_3P)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2(NO_3)_2$ in DMSO-d_6, at 27 °C. ^{31}P data vs. 85% H_3PO_4.

The simultaneous coordination of the NH_2-deprotonated nucleobase *either* through the N(6),N(7) or N(6),N(1) atoms, with formation of a chelated adduct, has been postulated by Rosenberg and coworkers in the interaction of *cis*-$PtCl_2(NH_3)_2$ with adenosine [9]. The spectrophotometric method used in that investigation did not resolve the dichotomy in the binding mode of the purine ring. The only structurally characterized example of an adeninate complex appears to be the *mononuclear* derivative $[Cp_2Mo(9\text{-}MeAd(-H))]PF_6$ ($Cp = \eta^5\text{-}C_5H_5$) obtained by reacting Cp_2MoCl_2 with 9-methyladenine. The kinetic product of the reaction contains the N(6),N(1)-chelated nucleobase, which at 80 °C isomerizes to the corresponding N(6),N(7) derivative [4].

Thus, in the interaction with *cis*-$[(PMe_3)_2Pt(\mu\text{-}OH)]_2(NO_3)_2$ 9-ethyladenine behaves similarly to 1-methylcytosine. For both the nucleobases, in fact, the hydroxo complex causes a facile deprotonation of the exocyclic amino group and the formation of 'isostructural' adducts. However, while the dinuclear complex *cis*-$[(Me_3P)_2Pt(\mu\text{-}1\text{-}MeCy(-H))]_2^{2+}$ in water or DMSO slowly converts into a thermodynamically more stable derivative, the trinuclear species *cis*-$[(Me_3P)_2Pt(\mu\text{-}1\text{-}MeCy(-H))]_3^{3+}$ [10], the adeninate complex $[(PMe_3)_2Pt(\mu\text{-}9\text{-}EtAd(-H))]_2^{2+}$ appears quite stable as shown by the invariance of its proton and phosphorus NMR spectra after several hours at 60 °C.

Supplementary material

Additional crystallographic material: a list of the bond lengths (Table A) and angles (Table B), the anisotropic displacement coefficients (Table C), and observed and calculated structure factors are available on request from the authors.

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References

1 B. Lippert, *Prog. Inorg. Chem.*, *37* (1989) 1, and references therein.

2 C.J.L. Lock, R.A. Speranzini, G. Turner and J. Powell, *J. Am. Chem. Soc.*, *98* (1976) 7865.

3 S. Jaworski, S. Menzer, B. Lippert and M. Sabat, *Inorg. Chim. Acta*, *205* (1993) 31.

4 L.Y. Kuo, M.G. Kanatzidis and T. Marks, *J. Am. Chem. Soc.*, *109* (1987) 7207.

5 (a) G. Trovó, G. Bandoli, U. Casellato, B. Corain, M. Nicolini and B. Longato, *Inorg. Chem.*, *29* (1990) 4616; (b) G. Trovó, B. Longato, *Inorg. Chim. Acta*, *192* (1992) 13; (c) G. Trovó, G. Valle and B. Longato, *J. Chem. Soc., Dalton Trans.*, (1993) 669.

6 *International Tables for X-ray Crystallography*, Vol. 4, Kynoch, Birmingham, UK, 1974.

7 G.M. Sheldrick, *SHELXTL-PLUS*. University of Göttingen, Germany, 1987.

8 P.C. Kong and T. Theophanides, *Inorg. Chem.*, *13* (1974) 1981.

9 S. Mansy, B. Rosenberg and A.J. Thomson, *J. Am. Chem. Soc.*, *95* (1973) 1633.

10 L. Schenetti, G. Trovó, G. Bandoli, A. Dolmella and B. Longato, manuscript in preparation.