Inorganica Chimica Acta, 205 (1993) 31–34

A trinuclear Pt adenine complex containing *cis*-$(NH_3)_2Pt^{II}$ bound to N1 and $(NH_3)_3Pt^{II}$ coordinated to N7

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(Received September 7, 1992)

Abstract

A compound of composition $[Pt_3(NH_3)_8(9\text{-MeA})_2](NO_3)_6\cdot 2H_2O$, where 9-MeA = 9-methyladenine, $C_6H_7N_5$, is reported which contains two $(NH_3)_3Pt^{II}$ residues bound to 9-MeA via N7 and a *cis*-$(NH_3)_2Pt^{II}$ entity bound to 9-MeA through N1. The two adenine rings are oriented head-to-head in the solid state, while in solution, an equilibrium between two rotamers (head–head, head–tail) exists. The X-ray structure is described, and based on it, the formation of related macrocyclic rings is proposed.

Introduction

In model studies concerned with reactions of metal ions or metal coordination compounds with nucleic acids usually single metal electrophiles are applied. The sequential application of different metal species is attractive in that it can lead to larger aggregates or eventually permit the preparation of species which otherwise are difficult to obtain [1]. For example, Ag^I links the neutral *trans*-$(NH_3)_2Pt(1\text{-MeU})_2$ (1-MeU = 1-methyluracil anion) into a polymer [2], and initial (dien)Pt^{II} binding to N7 of a guanine nucleobase eventually allows the preparation of N1 platinated species [3]. Applying this latter strategy to 9-methyladenine has led us to the trinuclear Pt^{II} complex *cis*-$\{(NH_3)_2Pt[(N1\text{-}9\text{-MeA-}N7)Pt(NH_3)_3]_2\}(NO_3)_6\cdot 2H_2O$, the structure of which is reported herewith. The compound, which may also be considered a model of a hypothetical A-*N*1,A-*N*1 adduct of *cis*-$(NH_3)_2Pt^{II}$ with DNA (head–head orientation of bases!), suggests that a related compound containing simultaneously *cis*- and *trans*-$(NH_3)_2Pt^{II}$ may be prepared and used as a building block for metallomacrocyclic ligands, which could be of interest as hosts for suitable organic ligands.

Experimental

Preparation

$[(NH_3)_3Pt(9\text{-MeA-}N7)]Cl_2$ [4] (0.5 mmol) was converted into the NO_3^- salt by treatment with $AgNO_3$ (1 mmol) in water, filtered from AgCl, and combined with *cis*-$[(NH_3)_2Pt(H_2O)_2](NO_3)_2$ (0.25 mmol), which was prepared *in situ* from *cis*-$(NH_3)_2PtCl_2$ and $AgNO_3$. The acidic solution (pH 2) was allowed to slowly evaporate at 22 °C. After several days, colorless crystals of the title compound were harvested in 43% yield. *Anal.* Calc. for $[Pt_3(NH_3)_8(C_6H_7N_5)_2](NO_3)_6\cdot 2H_2O$: C, 10.09; H, 2.97; N, 23.55; Pt, 40.99. Found: C, 10.0; H, 3.1; N, 23.0; Pt, 41.6%.

^1H NMR (D_2O, ppm, relative to internal TSP): 3.88, 3.89 ($N\text{-}CH_3$), 8.77, 8.78 (H8), 9.02, 9.05 (H2); ^1H NMR ($Me_2SO\text{-}d_6$, ppm, relative to TMS): 3.82, 3.85 ($N\text{-}CH_3$), 4.32, 4.61 ($(NH_3)_3$), 4.74 ($(NH_3)_2$), 8.85, 8.86 (H8), 9.05, 9.13 (H2), 9.26 (NH_2). Differentiation of H2 and H8 resonances by use of 9-MeA deuterated at 8-position. Raman (solid state, cm^{-1}): 287(1), 382(2), 544, 555(5), 726(4), 800(2), 950(0), 1053(10), 1087(0), 1204(0), 1234(1), 1314(5), 1362(2), 1391(6), 1430(0), 1450(0), 1475(1), 1486(1), 1518(1), 1550(2), 1592(2), 1660(0), 1677(0).

X-ray analysis

Crystal data and experimental details are given in Table 1. Preliminary investigations indicated an orthorhombic unit cell. Systematic absences of the type 0*kl*:

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0020-1693/93/$6.00

$k+1=2n$ and $hk0$: $h=2n$ suggested the centrosymmetric space group *Pnma* (No. 62) and non-centrosymmetric $Pn2_1a$, a non-standard setting of the space group $Pna^{2}{}_{1}$ (No. 33). The space group *Pnma* was assumed to be correct on the basis of the successful structure solution and refinement. Absorption corrections were applied by using the DIFABS program [5] with the transmission factors ranging from 0.88 to 1.20. Calculations were carried out on a VAX station 3520 using the TEXSAN crystallographic software package [6]. The structure was solved by direct methods (MITHRIL) [7]. Full-matrix parameters for all non-H atoms but those of the disordered nitrate groups yielded the final R of 0.049 ($R_w=0.065$). H atoms were introduced in the calculated positions without further refinement. The final difference Fourier map showed a peak 1.98 e/Å^3 located near one of the Pt atoms. Positional parameters are given in Table 2. For additional details, in particular the treatment of disordered nitrates, see 'Supplementary material'.

TABLE 1. Experimental details of X-ray structure determination

Crystal data	
Empirical formula	$Pt_3O_{20}N_{24}C_{12}H_{42}$
Formula weight	1427.88
Crystal color, habit	colorless, needle
Crystal dimensions (mm)	0.310 × 0.180 × 0.120
Crystal system	orthorhombic
Lattice parameters	
a (Å)	15.892(3)
b (Å)	23.292(5)
c (Å)	10.451(2)
V (Å^3)	3869(2)
Space group	*Pnma* (No 62)
Z value	4
D_{calc} (g/cm^3)	2.451
μ(Mo Kα) (cm^{-1})	110.36
Intensity measurements	
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo Kα ($\lambda=0.71069$ Å)
Temperature (°C)	−120
$2\theta_{max}$ (°)	48
Total reflections measured	3425
Corrections	Lorentz–polarization absorption (transmission factors 0.88–1.20)
Structure solution and refinement	
Structure solution	direct methods (MITHRIL)
Refinement	full-matrix least-squares
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
No. observations ($I>3.00\sigma(I)$)	2270
No. variables	254
Reflection/parameter ratio	8.94
Residuals: R; R_w	0.049; 0.065
Goodness of fit indicator	1.63
Maximum peak in final difference map (e$^-$/Å^3)	1.98

TABLE 2. Atomic coordinates and B_{eq}[a]

Atom	x	y	z	B_{eq}
Pt(1)	0.90881(6)	1/4	0.17470(9)	2.38(4)
Pt(2)	1.12330(4)	0.08700(3)	−0.21397(5)	2.71(3)
N(1)	0.820(1)	0.1865(7)	0.194(1)	4.4(8)
N(1A)	0.9968(8)	0.1870(5)	0.166(1)	2.8(6)
N(2)	1.032(1)	0.0231(7)	−0.215(1)	4.3(8)
N(3)	1.122(1)	0.0905(8)	−0.408(2)	5(1)
N(3A)	1.088(1)	0.1302(6)	0.298(1)	3.6(7)
N(4)	1.217(1)	0.1471(7)	−0.218(1)	4.9(8)
N(6A)	0.9898(8)	0.1782(5)	−0.058(1)	2.4(6)
N(7A)	1.1305(8)	0.0869(6)	−0.025(1)	3.0(6)
N(9A)	1.1749(8)	0.0649(6)	0.174(1)	3.0(6)
C(2A)	1.029(1)	0.1705(8)	0.278(2)	3.6(8)
C(4A)	1.114(1)	0.1072(7)	0.188(1)	2.3(7)
C(5A)	1.087(1)	0.1212(6)	0.068(1)	2.2(6)
C(6A)	1.021(1)	0.1618(7)	0.053(1)	2.7(7)
C(8A)	1.184(1)	0.0545(7)	0.043(1)	2.7(7)
C(9A)	1.219(1)	0.0371(8)	0.276(2)	3.8(8)
O(1W)	0.856(1)	1/4	−0.143(2)	3.7(8)
O(2W)	0.893(2)	1/4	0.603(2)	9(2)
N(11)	1.354(1)	0.0836(6)	−0.440(2)	4.0(8)
O(11)	1.365(1)	0.0762(6)	−0.325(1)	5.4(8)
O(12)	1.2950(9)	0.1108(9)	−0.482(1)	6.6(9)
O(13)	1.406(1)	0.0608(7)	−0.516(1)	6.0(8)
N(21A)	0.914(3)	0.036(2)	0.516(4)	5.1(7)
O(21A)	0.872(4)	0.055(3)	0.388(7)	13(1)
O(22A)	0.946(3)	0.090(2)	0.559(4)	8(1)
O(23A)	0.960(3)	0.011(2)	0.525(5)	11(1)
N(21B)	0.904(2)	0.078(2)	0.468(4)	4.4(7)
O(21B)	0.889(2)	0.084(1)	0.352(3)	4.6(6)
O(22B)	0.932(2)	0.119(1)	0.526(3)	5.2(7)
O(23B)	0.851(5)	0.055(4)	0.498(8)	20(2)
N(31)	0.704(2)	0.271(1)	0.446(3)	3.7(6)
O(31)	0.670(1)	1/4	0.542(2)	5.9(5)
O(32)	0.677(1)	1/4	0.337(2)	5.8(5)
O(33)	0.762(2)	0.312(1)	0.459(2)	4.3(5)
N(41)	0.620(4)	1/4	0.926(6)	14(1)
O(41)	0.679(2)	1/4	0.942(3)	10(2)
O(42)	0.570(2)	0.291(2)	0.915(3)	18(1)

[a] Occupancies 1/2 for Pt(1), O(1W), O(2W), N(21A)–O(41).

Spectroscopy

^{1}H NMR spectra (D_2O and Me_2SO-d_6) were obtained out on a Bruker AC200, instrument, with TSP and TMS internal standards, respectively. For variable temperature NMR spectra, a VT-1000-E unit was employed. Lineshape analyses were performed on an AT-IBM PC applying a self-developed program based on the theory of Gutowsky and Holm [8]. The Raman spectrum was recorded at a Coderg T800 instrument with Ar laser excitation (415.5 nm). Relative intensities refer to signal heights.

Results

Figure 1 gives a view of the cation of the title compound *cis*-$\{(NH_3)_2Pt[9\text{-MeA})Pt(NH_3)_3]_2\}(NO_3)_6\cdot$

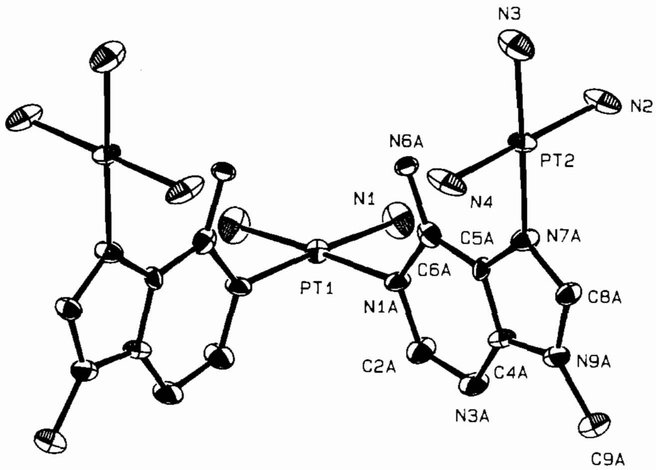

Fig. 1. View of the trinuclear cation of the title compound (30% ellipsoids). Selected structural details: Pt1–N1, 2.06(1) Å; Pt1–N1A, 2.03(1) Å; Pt2–N2, 2.08(2) Å; Pt2–N4, 2.05(2) Å; Pt2–N7A, 1.98(1) Å; N1–Pt1–N1, 91.8(9)°; N1–Pt1–N1A, 87.7(6)°; N1–Pt–N1A, 176.9(5)°; N1A–Pt1–N1A, 92.7(8)°; N2–Pt2–N3, 90.9(6)°; N2–Pt2–N4, 177.0(6)°; N2–Pt2–N7A, 92.5(5)°; N3–Pt2–N4, 88.0(6)°; N3–Pt2–N7A, 176.6(6)°; N4–Pt2–N7A, 88.6(6)°.

$2H_2O$. In accordance with the way of preparation, the monofunctional $(NH_3)_3Pt^{II}$ entities are coordinated through N7, and the bifunctional *cis*-$(NH_3)_2Pt^{II}$ binds to two adenines via N1. The central Pt atom is located on a mirror plane, with the two adenines arranged in a head–head fashion. Angles and distances about the metals (see legend of Fig. 1) are normal and compare well with other compounds containing $(NH_3)_3Pt^{II}$ or *cis*-$(NH_3)_2Pt^{II}$ entities [9, 10]. Errors in the adenine geometry are too large to justify a detailed comparison with the free base [11] or related Pt^{II}-μ-adenine complexes [12]. Relevant angles between Pt and 9-MeA planes in all cases are close to 90°, e.g. Pt1/9-MeA, 90.4°, Pt2/9-MeA, 89.2°, 9-MeA/9-MeA, 90.1°.

The Raman spectrum (solid state) of the title compound is dominated by intense bands due to $\nu_1 NO_3^-$ (1053 cm^{-1}), νPt–NH_3 (544 and 555 cm^{-1}) and 9-MeA ring modes (1391, 1362, 800, 726 cm^{-1}). Relative positions of the two 9-MeA bands in the 700–800 cm^{-1} range are sufficiently different from those of (9-MeA-*N*7)Pt^{II} and (9-MeA-*N*1)Pt^{II} species [1, 13] and are therefore suitable for rapid diagnostic purposes of the μ-*N*7,*N*1 binding mode of Pt^{II}.

In solution (D_2O or Me_2SO-d_6), the title compound exists as a mixture of two rotamers, as evident from ^1H NMR spectroscopy (doubling of H2/H8 and N-CH_3 resonances). Relative intensities are *c*. 0.4:0.6 (Me_2SO-d_6) and *c*. 0.35:0.65 (D_2O), respectively (Fig. 2(a)). Hindered rotation is probably around the Pt–N1 bond giving rise to head–head and head–tail isomers. The three NH_3 groups (Me_2SO-d_6) of the N7 bound Pt are split in a 2:1-ratio, as in the starting compound [4],

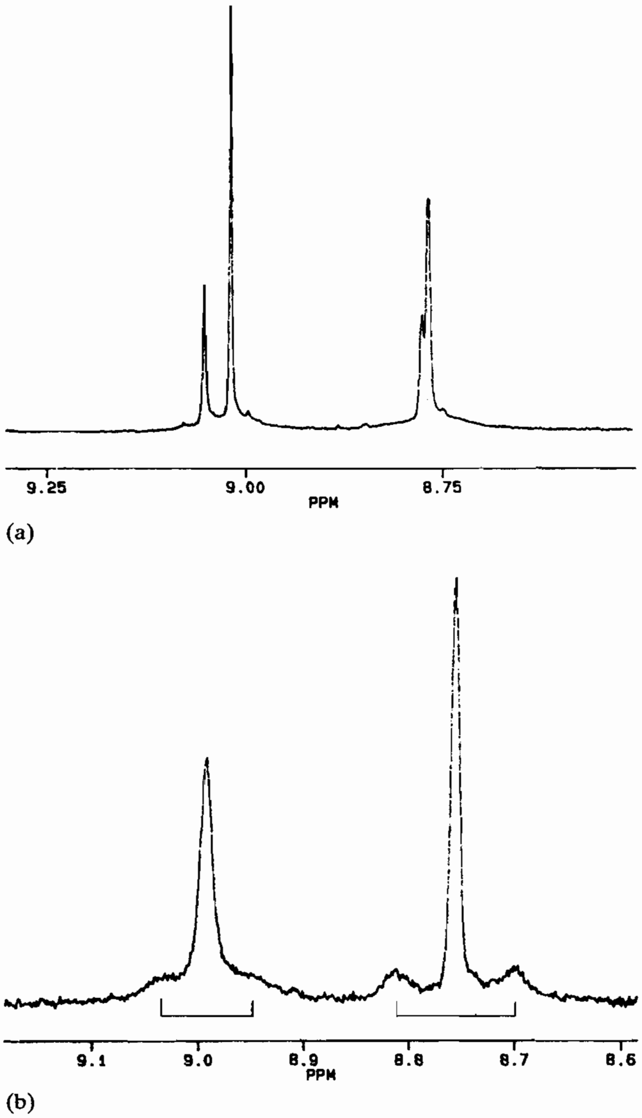

Fig. 2. ^1H NMR spectra (D_2O, aromatic region only) of (a) title compound at 285 K with two pairs of H2 (*c*. 9 ppm) and H8 (8.78 ppm) resonances, (b) title compound at 343 K with single averaged sets of H2 and H8 and ill-resolved ^{195}Pt satellites of 17 and 22 Hz, respectively.

and assigned to the NH_3 groups *cis* to N7 and *trans* to N7, respectively. Variable temperature ^1H NMR spectra in D_2O indicate a coalescence temperature of *c*. 330 ± 2 K for interconversion of the two rotamers. Above this temperature single averaged signals for H8 and H2 are observed, both of which display somewhat broadened ^{195}Pt satellites (Fig. 2(b)). $^3J(^{195}Pt–^1H)$ coupling constants are *c*. 22 Hz for the aromatic proton to higher field and *c*. 17 Hz for the aromatic proton to lower field under these conditions. Based on the geometry of the compound in the solid state, it would seem that the intracomplex stacking of the two adenines should cause the H2 resonances to be upfield relative to those of H8, but the actual assignment (made by

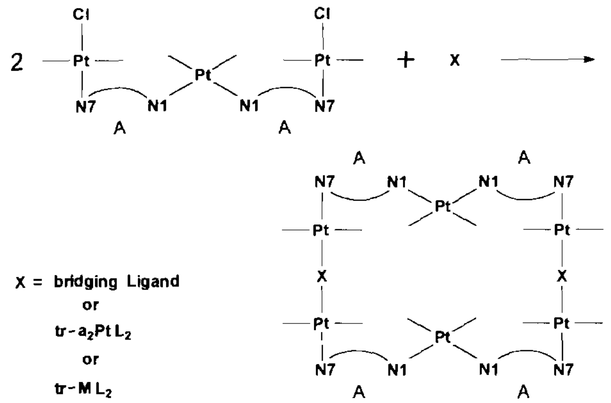

Fig. 3. Proposed reaction scheme for the preparation of macrocyclic metal complexes containing *cis*-a$_2$Pt^{II}, *trans*-a$_2$Pt^{II}, bridging adenines and bridging X entities.

use of the compound containing 9-MeA-D8) shows this not to be true. Lineshape analysis of the aromatic ^{1}H NMR signals gives a barrier of rotation of $\Delta H^{\neq}=76.5$ kJ mol^{-1} and $\Delta S^{\neq}=16.2$ JK^{-1} mol^{-1}. This barrier thus is very similar to that between two head–tail isomers (diastereomers) of (en)Pt(5′-dAMP-*N*7)$_2$ (71 ± 4 kJ mol^{-1}), which was also determined by ^{1}H NMR spectroscopy [14]. The calculated barrier of rotation about Pt–N7 in *cis*-[(NH$_3$)$_2$Pt(9-EtA-*N*7)$_2$]$^{2+}$ is lower, 39.6 kJ mol^{-1} [15].

Outlook

The structure of the trinuclear compound described here has prompted us to try to prepare a similar compound containing both *cis* and *trans*-(NH$_3$)$_2$Pt^{II}, the latter being coordinated via N7. The relative orientation of the two *trans*-Pt^{II} entities in a head–head complex should permit the synthesis of macrocyclic polynuclear complexes, containing at least 6–8 Pt atoms (Fig. 3). Compounds of this type should be candidates to function as 'inorganic hosts' for organic molecules [16]. Work in our laboratory is in progress to further explore this aspect.

Supplementary material

Details of the data collection, structure solution, atomic coordinates, displacement parameters, planes and a listing of observed and calculated structure factors can be obtained from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, under CSD 56589 on request. Requests should be accompanied by the complete literature citation.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and Asta Medica (loan of K$_2$PtCl$_4$). We thank M. Lutterbeck for the preparation of Fig. 3.

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