Inorganica Chimica Acta, 67 (1982) 151–158

A Second Modification of the Head-Tail Dimer Bis(μ-1-methylthyminato)-bis-(*cis*-diammineplatinum(II)) Dinitrate and its Differentiation from the Corresponding Head-Head Dimer

DIETMAR NEUGEBAUER and BERNHARD LIPPERT*

Anorganisch-Chemisches Institut der Technischen Universitat Munchen, Lichtenbergstrasse 4, D-8046 Garching, F R G.

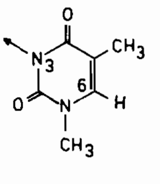
Received May 12, 1982

A compound containing two cis-$Pt(NH_3)_2^{2+}$ *moieties and two 1-methylthyminato ligands (1-MeT) in a head-tail arrangement has been prepared and the X-ray structure determined.* cis-$[Pt(NH_3)_2(C_6H_7N_2O_2)]_2(NO_3)_2\cdot 4.5H_2O$ *crystallizes in space group* $P\bar{1}$ *with the cell parameters* a = *11.32(1)* Å, b = *13.37(1)* Å, c = *22.63(1)* Å, α = *109.61(6)°,* β = *82.07(6)°,* γ = *115.58(7)°,* Z = *4. The structure was refined on 7304 reflections to* $R = R_w = 0.086$. *The crystallographic unit consists of two independent head-tail dimers with intramolecular Pt–Pt distances of 2.915 and 2.920 Å respectively, and intermolecular Pt–Pt distances of 3.878 and 3.964 Å. The dimers are linked by hydrogen bonds (2.895–3.054 Å) between the non-coordinating keto oxygens of 1-MeT and the two* NH_3 *groups of adjacent dimer units. Platinum binding occurs through N3 and O4 in all cases, and H-bonding through O2. The crystal structure of the title compound is different from a previously described head-tail dimer (monohydrate) with regard to intra- and intermolecular Pt–Pt separations. A differentiation of the title compound from the corresponding head-head dimer is possible on the basis of their different reactions with excess NaCl: while the head-head dimer is decomposed into equimolar amounts of* cis-$Pt(NH_3)_2(1\text{-}MeT)_2$ *and* cis-$Pt(NH_3)_2Cl_2$, *the head-tail dimer forms* cis-$Pt(NH_3)_2(1\text{-}MeT)Cl$ *as the sole product.*

Introduction

The interest in complexes of *cis*-Pt(II) with the model nucleobases 1-methyluracil and 1-methylthymine originates, among others [1], in the yet unresolved structure of 'platinum pyrimidine blues' [2–6]. Despite the full characterization of a crystalline blue platinum complex containing α-pyridone as ligand [7], the transformation of these results to N1 substituted or fully unsubstituted pyrimidine-2,4-diones with respect to coordination aspects remains questionable, due to the higher number of potential donor sites and combinations of these in the latter [8].

During the reaction of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with sodium 1-methylthyminate we obtained, among other products, yellow crystals of a Pt(II) dimer with two bridging 1-methylthyminato, (1-MeT), ligands in head-tail arrangement, *cis*-$[Pt(NH_3)_2(1\text{-MeT})]_2\cdot(NO_3)_2\cdot 4.5H_2O$. Alternately we isolated a second crystalline modification of this head-tail dimer from a solution of *cis*-$[Pt(NH_3)_2(1\text{-MeT})(H_2O)]NO_3$, prepared by reaction of *cis*-$Pt(NH_3)_2(1\text{-MeT})Cl\cdot H_2O$ [9] with $AgNO_3$ in water, which was identical with the monohydrate previously described by Lock, Rosenberg and co-workers [10]. An unambiguous crystallographic differentiation of the exocyclic oxygens of the 1-MeT ligands is not possible, due to the existence of the pseudo twofold axis through N3 and C6, but N3, O4 platinum binding gives the best fit with the experimental results. N3, O4 bridging has been found/assumed to occur in other di- and polynuclear 1-MeT complexes [11–15], and has been shown unambiguously to exist in several complexes of 1-methyluracil [16–18].



We herewith report the crystal structure of bis-(μ-1-methylthyminato-N3,O4)bis-(*cis*-diammineplatinum(II))dinitrate-4.5hydrate and on a method of differentiation between head-head and head-tail platinum dimers which is based on the easy cleavage of the Pt–O bond in the presence of chloride. This

---

[*] Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

is another example of the apparent ease by which Pt–nucleobase complexes crystallize in different modifications, previously observed by us with mixed chloro, 1-methylcytosine [19] and mixed thyminato, 1-methylcytosine complexes [20] of *cis*-Pt(II).

Experimental

Preparation

cis-$Pt(NH_3)_2Cl_2$ was prepared according to the method of Dhara [21] and recrystallized from DMF/aqueous HCl. The title compound was prepared as follows: 5 mmol of *cis*-$[Pt(NH_3)_2(H_2O)_2](NO_3)_2$, obtained *in situ* from *cis*-$Pt(NH_3)_2Cl_2$ and 2 $AgNO_3$ in water after filtration of AgCl, 20 mmol 1-methylthymine (Vega Biochemicals) and 7 mmol NaOH were stirred at 80 °C for 4.5 h. The total volume was 100 ml. The purple-black solution (pH 3.7) was filtered hot from an unidentified precipitate and concentrated to 30 ml volume. After filtration of 1.6 g of 1-methylthymine the solution was allowed to evaporate at room temperature. 100 mg of the previously described head-head dimer *cis*-$[Pt(NH_3)_2(1\text{-MeT})]_2(NO_3)_2$ [12] (yellow cubes, transparent on air) were collected first, then 200 mg of the title compound (yellow, transparent columns, rapidly loosing water of crystallization on air), later on 250 mg of a mixture of both compounds and of more unreacted 1-methylthymine. When the solution was dry, 1.55 g of a mixture, consisting predominantly of *cis*-$Pt(NH_3)_2(1\text{-MeT})_2 \cdot NaNO_3 \cdot (H_2O)_x$, was obtained.

The extremely fast loss of water of crystallization of the title compound did not permit performance of a reliable elemental analysis. This was therefore carried out with a sample kept on air until weight constancy was reached. *Anal.* Calcd. for $[Pt(NH_3)_2(C_6H_7N_2O_2)]_2(NO_3)_2 \cdot H_2O$. C, 16.40; H, 3.22; N, 15.94; O, 20.03; Pt, 44.41. Found: C, 16.38; H, 3.38; N, 15.72; O, 20.25; Pt, 44.5. Formulation of the title compound as 4.5-hydrate therefore was based on the results of the structure determination and the density measurements (*vide infra*).

In another preparation 0.5 mmol *cis*-$Pt(NH_3)_2(1\text{-MeT})Cl \cdot H_2O$ [9] and 0.5 mmol $AgNO_3$ were stirred in 10 ml water for 24 h at room temperature, the precipitated AgCl centrifuged and the resulting solution briefly warmed to 50 °C, then allowed to evaporate. Among other products, yellow crystals were isolated which stayed transparent in air and which had a density of 2.46. This density compares with the value of 2.47 for the head-tail dimer modification previously reported [10]. Although the cell constants of the isolated compound could not be determined due to twin formation, we obtained the corresponding 1-methyluracil compound in an analogous way and unambiguously identified it [22]. Moreover, recrystallization of the yellow, transparent 1-MeT product from water gave the title compound (4.5-hydrate) in low yield.

Surprisingly, we could not find suitable conditions of recrystallization to transfer our compound into the $P2_1/c$ product of Lock *et al.* [10]. In all cases only the starting material ($P\bar{1}$ product) was recovered. However, with the mixed thyminato, 1-methylcytosine complexes similar problems had been noticed by us [20].

Density Measurements

Like elemental analysis, the determination of the density of the title compound by flotation (CH_2I_2/CCl_4) presented a problem. Densities of the title compound ($P\bar{1}$) varied from 2.17 to 2.23, depending upon the degree of dehydration, which compare with the value of 2.15 expected for a 4.5 hydrate. A sample kept on air for several hours, which analyzed as a monohydrate (blind, broken crystals), gave $D \cong 2.3$, and this may explain the higher values found for the title compound. In contrast, the $P2_1/c$ product of Lock *et al.* [10], which is stable on air, gave a $D = 2.46$.

Apparatus

IR spectra were recorded as Nujol mulls (CsI windows) on a Perkin Elmer 580 grating spectrometer. ^1H NMR spectra were obtained on a Jeol JNM-FX 60 Fourier-transform spectrometer at 30 °C. The solvent was D_2O and $[N(CH_3)_4]BF_4$ was used as an internal reference. Shifts (δ scale) were calculated relative to sodium 3-(trimethylsilyl)propanesulfonate (3.1869 ppm upfield). pD values were obtained by adding 0.4 units to the pH meter reading.

Crystallography

For X-ray analysis a crystal (dimensions approximately 0.4 X 0.4 X 0.5 mm) was sealed in a capillary together with a drop of water. The cell parameters and the space group were determined by precession photographs and refined by centering 15 reflections ($2\theta \geqslant 15°$) on a Syntex $P2_1$ diffractometer. The crystal data are: $a = 11.32(1)$, $b = 13.37(1)$, $c = 22.63(1)$ Å, $\alpha = 109.61(6)°$, $\beta = 82.07(6)°$, $\gamma = 115.58(7)°$, $V = 2610.0$ Å^3, space group $P\bar{1}$, $Z = 4$, mol wt. 941.8, $D_c = 2.15$, D_m 2.2 g cm^{-3} (*cf.* text), μMo-K$_\alpha$ = 101.9 cm^{-1}. Intensity data of 8782 independent reflections were measured (Mo-K$_\alpha$ radiation, $\lambda = 0.71069$ Å, graphite monochromator, $2° \leqslant 2\theta \leqslant 48°$, ω = scan). After Lorentz and polarization corrections the structure was solved by the SHELX-system. The main difficulty of the structure determination arose from the fact that the four Pt atoms lay almost exactly on a line. After several assays, however, the best solution of the direct methods of the SHELX-system gave the heavy atoms, and the subsequent difference Fourier maps showed

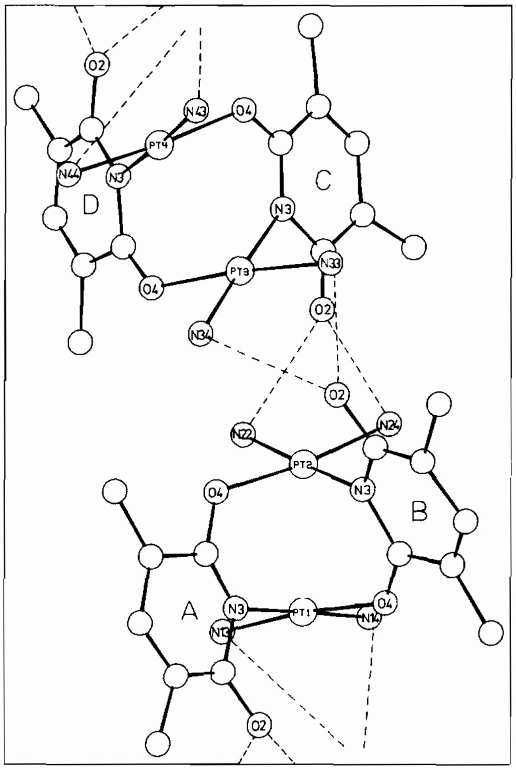


Fig. 1. The two crystallographically independent dimer cations of the title compound *cis*-$[Pt(NH_3)_2(1\text{-}MeT)]_2(NO_3)_2 \cdot 4.5H_2O$. Hydrogen bonding interactions are shown as dotted lines.

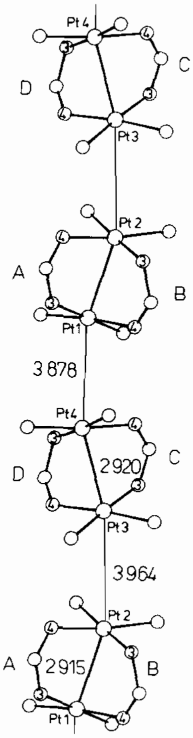


Fig. 2. The stacking of the dimer cations in the crystal. Pt atoms, NH_3 nitrogens and amidate linkages N3, C4, O4 are given only. Other atoms of the heterocyclic rings are omitted for clarity.

the positions of the light atoms. The structure was refined by full matrix least squares with anisotropic thermal parameters for the Pt atoms. The refinement of the temperature factors showed that the platinum atoms are bound to O4 of the 1-MeT ligands, and not to O2. With O4 binding, the temperature factors of N1 and C5 are as follows:

N1: 0.04644 (ligand A), 0.03890 (B); 0.04031 (C); 0.04754 (D); C5: 0.04558 (A); 0.03872 (B); 0.04695 (C): 0.04695 (D).

For the interchanged atomic coordinates the temperature factors are:

N1: 0.029060 (ligand A); 0.02190 (B); 0.02270 (C); 0.03090 (D); C5: 0.06100 (A); 0.05330 (B); 0.06420 (C); 0.07120 (D).

The hydrogen atoms were not located and the thermal parameters of the water oxygens and the nitrates showed that they are not exactly located. The final R value were $R = R_w = 0.086$ for 7304 reflections with $F_o \geq 2.0\ \sigma(F_o)$.

Results and Discussion

Structure

In Fig. 1 the two crystallographically independent dimer cations of the title compound are shown, and in Fig. 2 the arrangement of the dimers along the crystallographic y axis is depicted. For clarity, only the coordinating amidate units (N3–C4–O4) of the 1-MeT ligands are given in Fig. 2. Table I lists atomic parameters, in Tables II–IV selected interatomic distances, angles, and conformational parameters (as suggested by Orbell, Marzilli and Kistenmacher [24]), as well as possible hydrogen bonds are listed. Because of the relatively large errors, no comparison of 1-MeT ligand bond lengths and angles with those of the neutral 1-methylthymine [24] was undertaken. The cations consist of *cis*-diammineplatinum(II) units linked in a head-tail fashion by two 1-methylthiminato ligands through N3 and O4. The Pt atoms have square planar coordination spheres with slight deviations of the metals from the best planes (Table III), giving intermolecular Pt–Pt separations of 2.915(1) and 2.920(1) Å respectively. These Pt–Pt distances are shorter than the 2.974(1) Å found in the $P2_1/c$ modification [10], but slightly longer than in the head-head dimer (2.909(3) Å) [12]. Differences in the Pt–Pt separations are accompanied by differences in the tilt angles of the Pt coordination planes, being smallest in the head-head dimer (29.5°), largest in the head-tail-($P2_1/c$)-dimer (36.1°), and intermediate in the head-tail dimers of the $P\bar{1}$ product

TABLE I. Atomic Coordinates and Thermal Parameters.

Atom	x/a	y/b	z/c	U
Pt(1)	0.3730(1)	1.1758(1)	0.7356(1)	[a]
Pt(2)	0.3960(1)	0.9541(1)	0.6987(1)	[a]
Pt(3)	0.4383(1)	0.6833(1)	0.7122(1)	[a]
Pt(4)	0.4202(1)	0.4877(1)	0.7492	[a]
O(4B)	0.3164(19)	1.1108(16)	0.6453(9)	0.041(5)
N(3A)	0.1895(21)	1.0729(18)	0.7620(10)	0.029(5)
N(13)	0.4271(26)	1.2566(22)	0.8271(12)	0.048(6)
N(14)	0.5602(23)	1.2834(19)	0 7116(10)	0.039(5)
O(4A)	0.2399(19)	0.9218(16)	0.7575(8)	0.037(4)
N(22)	0.5124(23)	0.9887(19)	0.7689(10)	0.036(5)
N(3B)	0.2780(24)	0.9106(21)	0.6269(11)	0.040(6)
N(24)	0.5455(26)	0.9629(22)	0.6358(12)	0.046(7)
C(4A)	0.1652(28)	0.9770(23)	0.7702(13)	0.034(6)
C(51A)	0.0015(42)	0.7977(37)	0.8067(20)	0.080(11)
C(5A)	0.0372(32)	0.9140(27)	0.7975(14)	0.046(8)
C(6A)	−0.0514(35)	0.9691(29)	0.8092(16)	0.052(9)
N(1A)	−0.0195(22)	1.0669(18)	0.7963(10)	0.046(5)
C(11A)	−0.1107(40)	1.1239(35)	0.8141(19)	0.067(11)
C(2A)	0.0941(32)	1.1193(27)	0.7726(14)	0.045(7)
O(2A)	0.1235(21)	1.2141(18)	0.7596(10)	0.049(5)
C(4B)	0.2731(28)	1.0044(23)	0.6104(13)	0.036(6)
C(5B)	0.2076(29)	0.9706(24)	0.5510(13)	0.039(7)
C(51B)	0.1985(44)	1.0652(38)	0.5311(21)	0.078(12)
C(6B)	0.1568(34)	0.8679(29)	0.5161(16)	0.052(8)
N(1B)	0.1533(20)	0.7790(17)	0.5395(9)	0.039(5)
C(11B)	0.0977(38)	0.6504(32)	0.4971(17)	0.064(10)
C(2B)	0.2162(29)	0.8043(24)	0.5925(13)	0.036(7)
O(2B)	0.2135(23)	0.7253(20)	0.6122(11)	0.057(6)
O(4D)	0.4779(20)	0.7519(17)	0.8071(9)	0.042(5)
N(3C)	0.6261(23)	0.6893(19)	0.6911(10)	0.034(5)
N(33)	0.4018(24)	0.6304(20)	0.6181(11)	0.040(6)
N(34)	0.2516(24)	0.6791(21)	0.7301(11)	0.043(6)
N(3D)	0.5415(22)	0.6196(18)	0.8201(10)	0.035(5)
O(4C)	0.5713(19)	0.5068(16)	0.6893(9)	0.037(5)
N(43)	0.2933(24)	0.3491(21)	0.6804(11)	0.042(6)
N(44)	0.2747(24)	0.4645(20)	0.8143(11)	0.044(6)
C(4C)	0.6586(27)	0.6046(23)	0.6812(12)	0.034(6)
C(5C)	0.7850(33)	0.6167(28)	0.6605(15)	0.047(8)
C(51C)	0.8259(40)	0.5156(35)	0.6529(19)	0.071(11)
C(6C)	0.8681(40)	0.7153(35)	0.6500(19)	0.066(11)
N(1C)	0.8330(21)	0.8071(17)	0.6586(9)	0.040(5)
C(11C)	0.9204(38)	0.9037(32)	0.6364(17)	0.060(10)
C(2C)	0.7149(30)	0.8039(25)	0.6829(13)	0.038(7)
O(2C)	0.6835(19)	0.8786(16)	0.6936(8)	0.037(4)
C(4D)	0.5419(32)	0.7306(26)	0.8353(14)	0.043(7)
C(2D)	0.6188(28)	0.5971(24)	0.8471(13)	0.036(6)
O(2D)	0.6287(22)	0.4977(19)	0.8256(10)	0.053(6)
N(1D)	0.6943(22)	0.6823(19)	0.8972(10)	0.048(5)
C(11D)	0.7822(45)	0.6584(39)	0.9299(21)	0.084(13)
C(6D)	0.6877(35)	0.7873(30)	0.9193(16)	0.057(9)
C(5D)	0.6137(35)	0.8107(30)	0.8906(16)	0.054(9)
C(51D)	0.6073(38)	0.9331(33)	0.9144(18)	0.058(10)
N(50)	0.1470(37)	0.7744(34)	0.3265(18)	0.081(10)
O(51)	0.1079(37)	0.8315(34)	0.3690(19)	0.121(12)
O(52)	0.0882(37)	0.6653(34)	0.3047(18)	0.120(12)
O(53)	0.2441(29)	0.8188(25)	0.2915(14)	0.083(8)
N(60)	0.2819(136)	0.3538(112)	0.5037(63)	0.293(64)

(continued on facing page)

TABLE I. *(continued)*

Atom	x/a	y/b	z/c	U
O(61)	0.1857(58)	0.3608(49)	0.5059(26)	0.173(20)
O(62)	0.3546(38)	0.2947(33)	0.4564(18)	0.118(12)
O(63)	0.3850(57)	0.3768(49)	0.5520(27)	0.199(21)
N(70)	0.5556(57)	0.1709(54)	0.4975(28)	0.154(20)
O(71)	0.5419(47)	0.0868(43)	0.5339(23)	0.195(16)
O(72)	0.5367(45)	0.2682(42)	0.4838(22)	0.225(16)
O(73)	0.6226(46)	0.1999(43)	0.5764(23)	0.106(16)
N(80)	0.1699(76)	0.1945(77)	0.9117(36)	0.225(31)
O(81)	0.1816(58)	0.3121(57)	0.9095(28)	0.315(23)
O(82)	0.1242(64)	0.0808(55)	0.9389(28)	0.302(23)
O(83)	0.2630(64)	0.1068(52)	0.9191(28)	0.317(23)
O(90)	0.1316(27)	0.4376(24)	0.6313(13)	0.078(8)
O(91)	0.1213(31)	0.6008(27)	0.8425(15)	0.105(9)
O(92)	0.3400(30)	0.7700(27)	0.1484(14)	0.107(9)
O(93)	0.1368(33)	0.5437(29)	0.1887(16)	0.142(10)
O(94)	0.3676(34)	0.0307(30)	0.9044(16)	0.149(11)
O(95)	0.3872(35)	0.5443(31)	0.9496(17)	0.167(11)
O(96)	0.6196(35)	0.4146(31)	0.5272(17)	0.167(11)
O(97)	0.2248(36)	0.8117(32)	0.9464(17)	0.180(12)
O(98)	0.3949(36)	0.7779(32)	0.0218(17)	0.171(11)

[a] Anisotropic temperatures U_{ij} were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where β_{ij}'s occur as a temperature effect from $\exp[-(\beta_{11} h^2 + \ldots + 2\beta_{12} hk + \ldots)]$ and b_i and b_j are the reciprocal lattice vectors. For Pt(1), U_{11} = 29.5(7), U_{22} = 31.0(5), U_{33} = 42.8(6), U_{12} = 11.1(5), U_{13} = 1.1(5), U_{23} = 13.5(5), U_{11} = 27.9(7), U_{22} = 34.7(6), U_{33} = 36.9(6), U_{12} = 12.8(5), U_{13} = −0.4(5), U_{23} = 12.4(4), U_{11} = 29.2(7), U_{22} = 33.9(6), U_{33} = 39.8(6), U_{12} = 13.8(5), U_{13} = 5.0(5), U_{23} = 15.6(5), U_{11} = 38.1(7), U_{22} = 31.1(5), U_{33} = 33.4(6), U_{12} = 13.2(5), U_{13} = 1.6(5), U_{23} = 12.0(4).

TABLE II. Selected Interatomic Distances (Å) and Angles (deg) around the Pt Atoms.

Pt1–Pt2	2.915(1)		
Pt3–Pt4	2.920(1)		
Pt2–Pt3	3.964(1)		
Pt1–Pt4	3.878(1)		
Pt1–O4B	2.005(18)	Pt2–O4A	2.038(18)
N3A	2.075(21)	N3B	2.012(23)
N13	2.025(24)	N22	2.005(22)
N14	2.105(22)	N24	2.044(26)
Pt3–O4D	2.055(19)	Pt4–O4C	2.010(18)
N3C	2.087(22)	N3D	2.045(21)
N33	2.043(23)	N43	2.073(23)
N34	2.075(24)	N44	2.042(23)
(N14–Pt1–O4B)	90.4(8)	(N24–Pt2–O4A)	172.3(9)
(N14–Pt1–N3A)	178.3(8)	(N24–Pt2–N22)	91.5(10)
(N14–Pt1–N13)	88.4(9)	(N24–Pt2–N3B)	88.0(10)
(N13–Pt1–O4B)	173.8(9)	(N3B–Pt2–O4A)	90.8(8)
(N13–Pt1–N3A)	89.9(9)	(N3B–Pt2–N22)	177.0(9)
(N3A–Pt1–O4B)	91.2(8)	(N22–Pt2–O4A)	89.2(8)
(N34–Pt3–O4D)	89.6(8)	(N44–Pt4–N3D)	87.3(9)
(N34–Pt3–N3C)	177.7(9)	(N44–Pt4–O4C)	175.2(8)
(N34–Pt3–N33)	89.3(9)	(N44–Pt4–N43)	90.6(9)
(N33–Pt3–O4D)	174.6(8)	(N43–Pt4–N3D)	177.1(9)
(N33–Pt3–N3C)	88.8(9)	(N43–Pt4–O4C)	91.5(8)
(N3C–Pt3–O4D)	92.2(8)	(N3D–Pt4–O4C)	90.5(8)

TABLE III. Conformational Parameters of *cis*-[Pt(NH$_3$)$_2$(1-MeT)]$_2$(NO$_3$)$_2$·4.5H$_2$O.

(a) Dihedral angles (deg)

A/B	99.49		
C/D	109.51		
A/Pt(1)N$_3$O	93.16	C/Pt(3)N$_3$O	88.72
B/Pt(1)N$_3$O	117.02	D/Pt(3)N$_3$O	118.89
B/Pt(2)N$_3$O	95.05	D/Pt(4)N$_3$O	101.41
A/Pt(2)N$_3$O	111.75	C/Pt(4)N$_3$O	111.41

(b) Tilt angles (deg)

Pt(1)N$_3$O/Pt(2)N$_3$O	30.72
Pt(3)N$_3$O/Pt(4)N$_3$O	35.18

(c) Torsion angle about the Pt–Pt vectors (deg)

Pt1–Pt2	17.91
Pt3–Pt4	25.72

(d) Deviations (Å) of Pt atoms from least-squares coordination planes

ΔPt1	+0.0575	ΔPt3	−0.0584
ΔPt2	−0.0943	ΔPt4	+0.0563

TABLE IV. Possible Intermolecular Hydrogen Bonds.

(a) Between non-coordinating O2 of 1-MeT and NH$_3$ ligands

O2A–N43	2.895 Å	∠(Pt4–N43–O2A)	98.5°
N44	2.920	(Pt4–N44–O2A)	98.5
O2B–N33	2.949	(Pt3–N33–O2B)	103.0
N34	3.054	(Pt3–N34–O2B)	98.8
O2C–N22	2.947	(Pt2–N22–O2C)	97.6
N24	2.913	(Pt2–N24–O2C)	97.7
O2D–N13	3.050	(Pt1–N13–O2D)	102.3
N14	3.021	(Pt1–N14–O2D)	101.2

(b) Between H$_2$O and NH$_3$ groups

N13–O92	2.955 Å	x(Pt1–N13–O92)	110.4°
N22–O92	2.975	(Pt2–N22–O92)	122.3
N34–O91	3.023	(Pt3–N34–O91)	114.3
N43–O90[a]	3.049	(Pt4–N43–O90)	108.2
N44–O91[a]	2.895	(Pt4–N44–O91)	120.1
N44–O95	3.138	(Pt4–N44–O95)	111.7
N22–O94	3.264	(Pt2–N22–O94)	111.5
N33–O90	3.090	(Pt3–N33–O90)	91.5

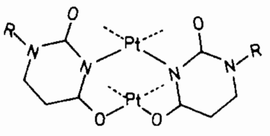
[a] Symmetry transformation: x; 1 + y; z.

(30.7 and 35.2°). In contrast to the head-head 1-MeT dimer, where the NH$_3$ groups of the two Pt atoms lie practically above each other (torsional angles 0.4–1.7°), the Pt coordination planes are rotated about the Pt–Pt vector by 13–14.5° in the $P2_1/c$ compound and 17.9° and 25.7° in the $P\bar{1}$ compound.

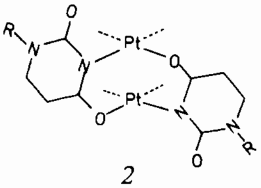
The main difference between the two head-tail dimer modifications is in the intermolecular arrangements of the dimers in the crystals: in the earlier compound adjacent dimers are separated by almost 6 Å (nearest Pt–Pt distance), whereas here in the described compound dimers are less than 4 Å apart and are held together by extensive interdimer hydrogen bonding (Fig. 1). Each non-coordinating keto oxygen O2 of the 1-MeT ligands is in a position to form two strong hydrogen bonds (2.9–3.05 Å), thus leading to a maximum of eight hydrogen bonds between one dimer and its two neighbours. The resulting arrangement – stacking of Pt$_2$ units along one axis –thus has some similarity with the structures of pyrophosphato-bis(*cis*-diammineplatinum(II)) [25] and tetrakis(dithioacetato)diplatinum(II) [26].

Spectroscopy

A differentiation between the head-head dimer *1* [12] and the head-tail dimer *2* by IR and ^{1}H NMR spectroscopy has been attempted. Although differences are observed in the IR spectra, which refer to 1-MeT modes (*e.g. 1*: 1515, 1500 vs; *2*: 1510 vs; *1*: 870 m,b; *2*: 850 m,b, 800 m,b), skeletal modes (*e.g. 1*: 545 m, 512 m; *2*: 540, 545m, 518s; *1*: 335 m, 320 m; *2*: 342 m) and to the OH stretching region (*2*: 3430 vs), these, as well as other minor differences do not permit the two compounds to be readily differentiated by this method. Crystal packing forces and hydrogen bonding effects could also be responsible for differences of this magnitude.

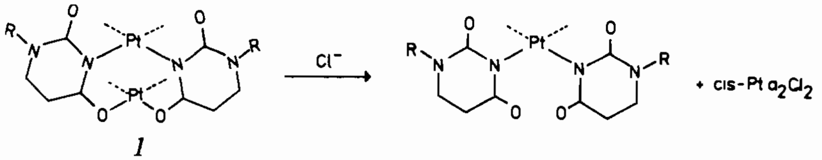


1



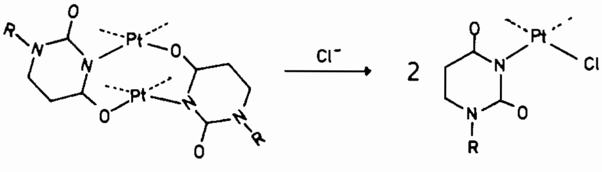
2

^{1}H NMR spectra of the two compounds do not differ greatly, and resonance of *1* and *2* occur within 0.01–0.02 ppm of each other in D$_2$O. We were able, however, to differentiate between the compounds *1* and *2* by adding excess NaCl to an aqueous solution of either compound, *cf.* diagrams on facing page. With *1* the appearance of signals due to *cis*-Pt(NH$_3$)$_2$(1-MeT)$_2$ upfield of the original ones of *1*, and the precipitation of *cis*-Pt(NH$_3$)$_2$Cl$_2$ were observed (Fig. 3). In contrast, the head-tail dimer *2*, with excess NaCl, gave the rather insoluble, almost colorless *cis*-Pt(NH$_3$)$_2$(1-MeT)Cl·D$_2$O, which was isolated from solution and identified by comparison with the identical compound obtained by reaction of *cis*-Pt(NH$_3$)$_2$(1-MeT)$_2$ with HCl [9]. In the NMR spectrum of *2*, on addition of NaCl a



1

decrease in the intensities of the original signals was observed. No distinct new signals were observed since the chemical shifts of the H resonances of *2* and the product formed are virtually identical.



2

There is definitely no *cis*-Pt(NH$_3$)$_2$(1-MeT)$_2$ formed as with *1*, nor any *cis*-Pt(NH$_3$)$_2$Cl$_2$.

The structure presented here provides an example of how long-range intermolecular hydrogen bonding interactions between non-coordinating oxygens of pyrimidine-2,4-diones and the NH$_3$ groups of *cis*-Pt(II) can occur in the solid state, and conceivably in solution as well. This pattern is by no means restricted to Pt dimers with head-tail arranged uracil and thymine ligands, and may play an important role in reinforcing metal–metal interactions in platinum blues.

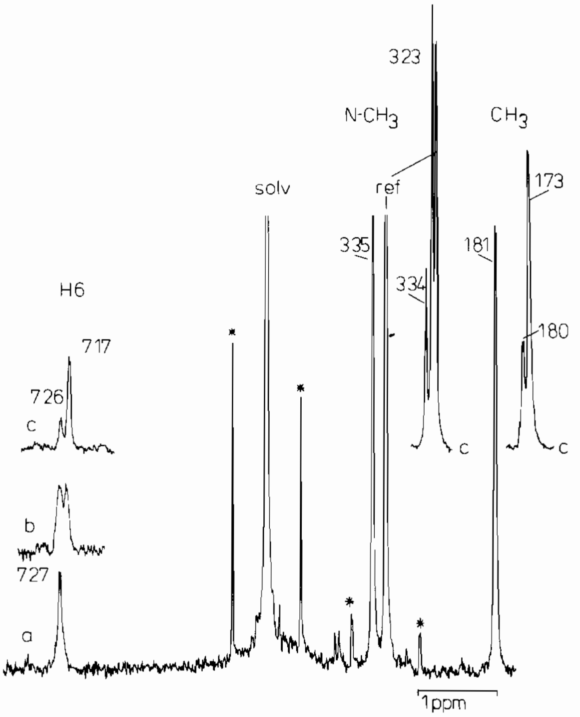


Fig. 3. ^{1}H NMR spectra (D$_2$O) of (a) head-head dimer *cis*-[Pt(NH$_3$)$_2$(1-MeT)]$_2$(NO$_3$)$_2$, 0.15 *M* Pt, pD = 4.4 (b) 20 h after addition of NaCl (1.5 *M* Cl$^-$), 22 °C. (c) 5 d after addition of NaCl, 22 °C. New signals at 7.17, 3.25, 1.73 ppm are due to *cis*-Pt(NH$_3$)$_2$(1-MeT)$_2$. Samples (b) and (c) contain yellow precipitate of *cis*-Pt(NH$_3$)$_2$Cl$_2$. ref = [NMe$_4$]$^+$; * spinning side bands.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft, DFG, and the Technische Universitat München for financial support of this work.

References

1 For recent reviews on metal ion–nucleobase interactions, see *e.g* various articles in 'Metal Ions in Biological Systems', H. Sigel, ed., Marcel Dekker, New York, 1980, Vols. 10 and 11, and 'Nucleic Acid–Metal Ion Interactions', T. G. Spiro, ed., Wiley, New York, 1980, Vol. 1.

2 J. P. Davidson, P. J. Faber, R. G. Fischer, S. Mansy, H. J. Peresie, B. Rosenberg and L. Van Camp, *Cancer Chemother. Rep , Part 1, 59,* 287 (1975).

3 R. J. Speer, H. Ridgway, L. M. Hall, D. P. Stewart, K. E. Howe, D. Z. Lieberman, A. D. Newman and J. M. Hill, *Cancer Chemother Rep , Part 1, 59,* 629 (1975).

4 C. M. Flynn, T. S. Viswanathan and R. B. Martin, *J. Inorg. Nucl Chem., 39,* 437 (1977).

5 B. Lippert, *J. Clin. Hematol Oncol , 7,* 26 (1977).

6 A J. Thomson, I. A. G. Roos and R. D. Graham, *J Clin. Hematol. Oncol., 7,* 242 (1977).

7 (a) J. K. Barton, H. N. Rabinowitz, D. J. Szalda and J. S. Lippard, *J Am. Chem. Soc., 99,* 2827 (1977);
(b) J. K. Barton, D. J. Szalda, H. N. Rabinowitz, J. V. Waszcazk and S. J. Lippard, *Idem, 101,* 1434 (1979);
(c) J. K. Barton, S. A. Best, S. J. Lippard and R. A. Walton, *Idem, 100,* 3785 (1978);
(d) J. K. Barton, C. Caravana and S. J. Lippard, *Idem, 101,* 7269 (1979).

8 B. Lippert, *Inorg. Chem., 20,* 4326 (1981).

9 B. Lippert, *Inorg. Chim Acta, 55,* 5 (1981).

10 C. J. L. Lock, H. J. Peresie, B. Rosenberg and G. Turner, *J. Am. Chem. Soc., 100,* 3371 (1978).

11 F. Guay and A. L. Beauchamp, *J. Am. Chem Soc., 101,* 6260 (1979).

12 B. Lippert, D. Neugebauer and U. Schubert, *Inorg. Chim. Acta, 46,* L11 (1980).

13 B. Lippert and D. Neugebauer, *Inorg. Chim. Acta, 46,* 171 (1980)

14 B. Lippert and U. Schubert, *Inorg. Chim. Acta, 56,* 15 (1981).

15 F. Guay and A. L. Beauchamp, *Inorg Chim Acta, 66,* 57 (1982).

16 R. Faggiani, C. J. L. Lock, R. J. Pollock, B. Rosenberg and G. Turner, *Inorg. Chem., 20,* 804 (1981).

17 B. Lippert and D. Neugebauer, *Inorg Chem.*, *21*, 451 (1982).

18 D. Neugebauer and B. Lippert, *J. Am. Chem. Soc.*, in press.

19 B. Lippert, C. J. L. Lock and R. A. Speranzini, *Inorg Chem.*, *20*, 335 (1981).

20 (a) R. Faggiani, B. Lippert, C. J. L. Lock and R. Pfab, *Inorg. Chem.*, *20*, 2381 (1981),
(b) B. Lippert, R. Pfab and D Neugebauer, *Inorg Chim Acta*, *37*, L495 (1979).

21 S. C. Dhara, *Indian J. Chem.*, *8*, 143 (1970).

22 D. Neugebauer and B. Lippert, to be published.

23 J. D. Orbell, L. G Marzilli and T. J Kistenmacher, *J. Am Chem Soc*, *103*, 5126 (1981).

24 K. Hoogsteen, *Acta Cryst.*, *16*, 28 (1963).

25 J A. Stanko, cited in 'Platinum Coordination Complexes in Cancer Chemotherapy', T. A. Connors and J. J. Roberts, eds., Springer, Berlin, 1974, p. 25.

26 C. Bellito, A. Flamini, O. Piovesana and P. F. Zanazzi, *Inorg Chem*, *19*, 3623 (1980)