A mixed Pt_2Tl complex of 1-methylthymine: structural evidence for the stereoactivity of the Tl^I electron lone pair and unexpected intracomplex nucleobase stacking

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Abstract

A trinuclear $Pt^{II}Tl^{I}Pt^{II}$ complex with bridging 1-methylthyminato (1-MeT) nucleobases, *cis*-$[(NH_3)_2Pt(1\text{-MeT})_2Tl(1\text{-MeT})_2Pt(NH_3)_2]NO_3 \cdot 7H_2O$, has been prepared and structurally characterized. It crystallizes in the space group $C2/c$ with $a=17.854(4)$, $b=23.063(5)$, $c=11.813(2)$ Å, $\beta=94.90(3)°$, $V=4846(2)$ Å^3, $Z=4$. The structure was refined on 3949 reflections to $R=0.0448$, $R_w=0.0564$. Pt^{II} binding is through the N3 positions of the 1-MeT rings, while Tl^I is bound via four exocyclic O4 oxygens. Pt–Tl separations (3.085(1)Å) are sufficiently short to postulate bonds between the two metals. The compound, which represents a rare example of a d^8–s^2–d^8 metal assembly, displays structural features indicative of a stereoactive electron lone pair at the central Tl^I. Unlike all previously studied related $Pt^{II}MPt^{II}$ complexes, for the first time intramolecular stacking between two of the four nucleobases is observed. This fact and the cleft at the Tl^I appear to be interrelated.

Introduction

Our interest in metal–nucleobase interactions has led us, among others, also to di- and multinuclear complexes [1]. Off all nucleobases, specifically the pyrimidine bases cytosine, thymine and uracil** appear to have a pronounced tendency to form multinuclear compounds [2], frequently displaying metal–metal bonds [1, 3]. Nucleobase complexes of these ligands with a strongly fixed, kinetically inert metal ion such as Pt^{II} proved to be particularly suitable for the preparation of di- or multinuclear compounds. Some of the aspects of these compounds, which we are interested in, are the extent of metal–metal interaction [1], oxidizability of the metals [1], stabilization of unusual oxidation states [4], interligand effects [5] and pharmacology [6]. Much of our work has been devoted to mixed-metal systems containing transition metals, e.g. combinations of Pt^{II} with Pd^{II}, Ag^{I}, Cu^{II} etc. Our choice of the main group ion Tl^I originally resulted from attempts to abstract Cl ligands by use of Tl^I from Cl containing Pt nucleobase complexes such as *cis*-$[(NH_3)_2Pt(1\text{-MeT})_2Pt(NH_3)Cl]^+$ [7]. Reaction products proved to be quite complex, however, with only the here described compound unambiguously characterized at present. It was subsequently obtained in a straightforward manner by cocrystallizing *cis*-$(NH_3)_2Pt(1\text{-MeT})_2$ and $TlNO_3$.

Two aspects of the chemistry of Tl^I [8] appeared to be of potential relevance to our compound, namely the question of the stereoactivity of the $6s^2$ lone electron pair [8, 9] and possible luminescence properties of Tl^I containing mixed-metal complexes [10], especially in combination with Pt^{II} [11]. As to the first aspect, in a recently performed X-ray structure analysis of a Tl^I–1-methylcytosine complex no evidence for a stereoactive $6s^2$ orbital had been found [12].

Experimental

cis-$(NH_3)_2Pt(1\text{-MeT})_2$ was obtained as previously described [13]. The title compound was prepared by reacting 0.1 mmol of *cis*-$(NH_3)_2Pt(1\text{-MeT})_2$ with 0.1 mmol $TlNO_3$ in 15 ml H_2O. Slow evaporation at room temperature over 10 days gave colorless, transparent single crystals suitable for X-ray crystallography. Variation of the Pt/Tl ratio did not yield another product. Yield 74%. *Anal.* Calc. for $[(NH_3)_2Pt(1\text{-MeT})_2Tl(1\text{-$

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**Abbreviations: 1-MeT = 1-methylthymine anion, 1-MeU = 1-methyluracil anion.

MeT)$_2$Pt(NH$_3$)$_2$]NO$_3\cdot$7H$_2$O ($Pt_2TlC_{24}H_{54}N_{13}O_{18}$): C, 20.48; H, 3.87; N, 12.94. Found: C, 20.2; H, 3.9; N, 12.7%.

The 1-MeU analogue was prepared similarly from *cis*-(NH$_3$)$_2$Pt(1-MeU)$_2$ [14], but the colorless crystals were not suitable for X-ray crystallography. Yield 70%. *Anal.* Calc. for [(NH$_3$)$_2$Pt(1-MeU)$_2$Tl(1-MeU)$_2$-Pt(NH$_3$)$_2$]NO$_3\cdot$8H$_2$O ($Pt_2TlC_{20}H_{48}N_{13}O_{20}$): C, 17.54; H, 3.53; N, 13.30. Found: C, 17.5; H, 3.4; N, 13.2%.

IR spectra (KBr pellets) were taken on a Perkin-Elmer 580B spectrometer, and Raman spectra on a Coderg T800 spectrometer using Ar$^+$ laser excitation (514.5 nm). ^{1}H NMR spectra were recorded on a Bruker AM300 spectrometer using D$_2$O (with TSP as internal reference).

For the structure determination, a crystal of size 0.30×0.25×0.09 mm, sealed in a capillary, was used. Details of the X-ray data collection are as follows: monoclinic space group *C2/c*, $a=17.854(4)$, $b=23.063(5)$, $c=11.813(2)$ Å, $\beta=94.90(3)°$, $V=4846(2)$ Å, $Z=4$, $\mu=9.165$ mm^{-1}, $F(000)=2872$, $D_c=2.060$ M gm^{-3}; Nicolet P2$_1$ diffractometer, graphite monochromated Mo Kα radiation (0.71073 Å) and ω-scan mode. Accurate unit-cell parameters were obtained by least-squares fit of 25 reflections ($8°<2\Theta<22°$). A total of 5176 reflections ($3.0°<2\Theta<53.0°$) of which 5023 unique ($R_{int}=1.9\%$) were collected with index ranges $0\leqslant h\leqslant 22$, $0\leqslant k\leqslant 28$ and $-14\leqslant l\leqslant 14$ resulted in 3946 observed ($F>6.0\sigma(F)$) reflections. The data were corrected for Lorentz and polarization effects and empirical absorption correction was made from ϕ-scan data (transmission 1.000–0.210).

The structure was solved by heavy atom and Fourier methods of the SHELXTL-Plus package [15] and refined by full-matrix least-squares with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were introduced in the calculated positions and refined with fixed geometry in respect to their carrier atoms. Final $R=0.0448$, $R_w=0.0564$, $S=1.43$ for 291 variables, with weighting scheme $w^{-1}=(F)+0.001(F)^2$. Maximum and minimum peaks in the final difference Fourier synthesis were 3.02 and -2.42 e Å^{-3} in the vicinity of the Tl atom and largest $\Delta/\sigma=0.781$. Final coordinates and U_{eq} are listed in Table 1.

Results and discussion

The molecular cation of the title compound and the atom numbering scheme are shown in Fig. 1. Interatomic distances and angles are listed in Table 2. The cation consists of two bis(1-methylthyminato-*N3*)-*cis*-diammineplatinum(II) units which are linked together by the heterometal ion Tl^I via four exocyclic oxygens of the four 1-MeT rings. The compound extends the list

TABLE 1. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3)

	x	y	z	U_{eq}
Tl(1)	5000	6985(1)	2500	51(1)
Pt(1)	3522(1)	7479(1)	1342(1)	35(1)
N(2)	3237(4)	6693(3)	636(6)	50(2)
N(1)	4178(4)	7644(3)	12(6)	49(2)
N(3A)	2835(3)	7303(3)	2607(5)	39(2)
C(4A)	3002(5)	6854(4)	3341(7)	49(3)
O(4A)	3587(4)	6561(3)	3268(6)	67(2)
C(5A)	2490(5)	6732(4)	4178(7)	51(3)
C(5A′)	2639(7)	6228(6)	4944(9)	74(4)
C(6A)	1874(5)	7061(5)	4222(8)	58(3)
N(1A)	1707(5)	7493(3)	3437(7)	55(3)
C(1A′)	979(5)	7805(6)	3449(11)	73(4)
C(2A)	2187(5)	7615(4)	2605(7)	43(3)
O(2A)	2012(3)	7984(3)	1865(5)	56(2)
N(3B)	3786(3)	8280(3)	2025(5)	38(2)
C(4B)	4155(4)	8343(4)	3086(6)	39(2)
O(4B)	4384(3)	7906(3)	3642(4)	44(2)
C(5B)	4259(4)	8924(4)	3524(7)	42(2)
C(5B′)	4644(5)	9016(4)	4685(7)	54(3)
C(6B)	4027(5)	9362(4)	2863(7)	51(3)
N(1B)	3691(4)	9290(3)	1787(6)	51(2)
C(1B′)	3483(7)	9792(4)	1062(9)	73(4)
C(2B)	3562(4)	8742(4)	1356(6)	45(3)
O(2B)	3256(3)	8680(3)	378(4)	52(2)
N(21)^a	5000	1226(9)	2500	97(8)
O(22)^a	5000	680(7)	2500	111(6)
O(21)	4420(7)	1498(5)	2668(10)	125(5)
O(1)	600(9)	659(7)	926(16)	199(9)
O(2)	1247(10)	237(7)	4882(15)	190(9)
O(3)	3173(7)	874(5)	3230(7)	110(4)
O(4)	1684(7)	841(5)	6932(10)	115(5)
O(5)	287(7)	1390(5)	5356(12)	141(6)
O(6)^a	0	832(12)	7500	213(15)
O(7)	2155(12)	39(9)	3295(14)	254(13)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. ^{a}The population parameter 0.5000.

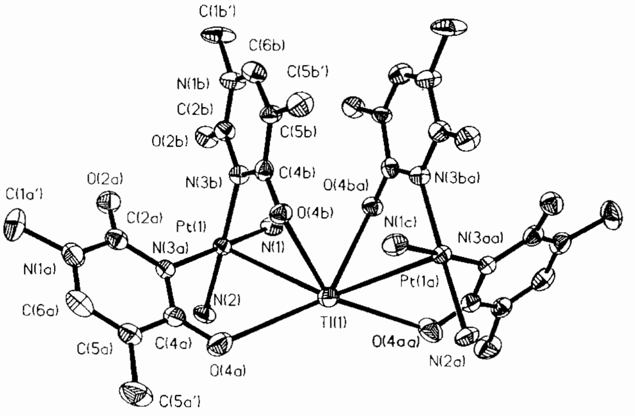

Fig. 1. View of the trinuclear cation of the title compound.

TABLE 2. Distances (Å) and angles (°) in the title compound

Tl(1)–Pt(1)	3.085(1)	Tl(1)–O(4A)	2.921(7)
Tl(1)–O(4B)	2.791(6)	Tl(1)–Pt(1A)	3.085(1)
Tl(1)–O(4AA)	2.921(7)	Tl(1)–O(4BA)	2.791(6)
Pt(1)–N(2)	2.043(7)	Pt(1)–N(1)	2.074(8)
Pt(1)–N(3A)	2.053(7)	Pt(1)–N(3B)	2.053(7)
N(3A)–C(4A)	1.368(11)	N(3A)–C(2A)	1.363(11)
C(4A)–O(4A)	1.253(11)	C(4A)–C(5A)	1.431(13)
C(5A)–C(5A′)	1.483(15)	C(5A)–C(6A)	1.341(14)
C(6A)–N(1A)	1.376(13)	N(1A)–C(1A′)	1.487(14)
N(1A)–C(2A)	1.388(12)	C(2A)–O(2A)	1.240(10)
N(3B)–C(4B)	1.373(9)	N(3B)–C(2B)	1.367(11)
C(4B)–O(4B)	1.254(10)	C(4B)–C(5B)	1.442(12)
C(5B)–C(5B′)	1.496(11)	C(5B)–C(6B)	1.322(12)
C(6B)–N(1B)	1.369(11)	N(1B)–C(1B′)	1.469(13)
N(1B)–C(2B)	1.375(12)	C(2B)–O(2B)	1.244(9)
N(21)–O(22)	1.260(25)	N(21)–O(21)	1.240(16)
N(21)–O(21A)	1.240(16)		
Pt(1)–Tl(1)–O(4A)	62.1(1)	Pt(1)–Tl(1)–O(4B)	64.9(1)
O(4A)–Tl(1)–O(4B)	73.6(2)	Pt(1)–Tl(1)–Pt(1A)	136.7(1)
O(4A)–Tl(1)–Pt(1A)	135.6(1)	O(4B)–Tl(1)–Pt(1A)	82.1(1)
Pt(1)–Tl(1)–O(4AA)	135.6(1)	O(4A)–Tl(1)–O(4AA)	140.9(3)
O(4B)–Tl(1)–O(4AA)	142.3(2)	Pt(1A)–Tl(1)–O(4AA)	62.1(1)
Pt(1)–Tl(1)–O(4BA)	82.1(1)	O(4A)–Tl(1)–O(4BA)	142.3(2)
O(4B)–Tl(1)–O(4BA)	81.0(2)	Pt(1A)–Tl(1)–O(4BA)	64.9(1)
O(4AA)–Tl(1)–O(4BA)	73.6(2)	Tl(1)–Pt(1)–N(2)	91.6(2)
Tl(1)–Pt(1)–N(1)	83.5(2)	N(2)–Pt(1)–N(1)	89.5(3)
Tl(1)–Pt(1)–N(3A)	98.4(2)	N(2)–Pt(1)–N(3A)	88.7(3)
N(1)–Pt(1)–N(3A)	177.5(3)	Tl(1)–Pt(1)–N(3B)	89.9(2)
N(2)–Pt(1)–N(3B)	178.5(3)	N(1)–Pt(1)–N(3B)	90.4(3)
N(3A)–Pt(1)–N(3B)	91.3(3)	Pt(1)–N(3A)–C(4A)	120.0(5)
Pt(1)–N(3A)–C(2A)	117.1(5)	C(4A)–N(3A)–C(2A)	122.7(7)
N(3A)–C(4A)–O(4A)	120.1(8)	N(3A)–C(4A)–C(5A)	118.0(8)
O(4A)–C(4A)–C(5A)	121.9(8)	Tl(1)–O(4A)–C(4A)	126.1(6)
C(4A)–C(5A)–C(5A′)	118.9(9)	C(4A)–C(5A)–C(6A)	119.3(9)
C(5A′)–C(5A)–C(6A)	121.7(9)	C(5A)–C(6A)–N(1A)	121.0(9)
C(6A)–N(1A)–C(1A′)	119.0(9)	C(6A)–N(1A)–C(2A)	120.9(8)
C(1A′)–N(1A)–C(2A)	120.0(8)	N(3A)–C(2A)–N(1A)	117.9(7)
N(3A)–C(2A)–O(2A)	121.7(8)	N(1A)–C(2A)–O(2A)	120.4(8)
Pt(1)–N(3B)–C(4B)	122.1(5)	Pt(1)–N(3B)–C(2B)	115.3(5)
C(4B)–N(3B)–C(2B)	122.6(7)	N(3B)–C(4B)–O(4B)	120.2(7)
N(3B)–C(4B)–C(5B)	117.6(7)	O(4B)–C(4B)–C(5B)	122.2(7)
Tl(1)–O(4B)–C(4B)	118.9(5)	C(4B)–C(5B)–C(5B′)	119.7(7)
C(4B)–C(5B)–C(6B)	118.3(7)	C(5B′)–C(5B)–C(6B)	121.9(8)
C(5B)–C(6B)–N(1B)	123.1(8)	C(6B)–N(1B)–C(1B′)	120.9(8)
C(6B)–N(1B)–C(2B)	120.1(7)	C(1B′)–N(1B)–C(2B)	118.9(7)
C(3B)–C(2B)–N(1B)	118.2(6)	N(3B)–C(2B)–O(2B)	122.1(8)
N(1B)–C(2B)–O(2B)	119.8(8)	O(22)–N(21)–O(21)	120.3(10)
O(22)–N(21)–O(21A)	120.3(10)	O(21)–N(21)–O(21A)	119.3(20)

of related trinuclear PtMPt species (M = Ag^{I} [16], Mn^{II} [17], Pd^{II} and Pd^{III} [18], Cu^{II} [19]) which we have previously structurally characterized. These known compounds can be categorized into two types. (i) The heterometal M has a square-planar or – with Pt acting as a ligand – an octahedral coordination geometry, e.g. with M = Mn^{II}, Pd^{II}, Pd^{III} and Cu^{II}. In these compounds, the three metals are colinear, the nucleobase planes are close to perpendicular to the Pt coordination planes, and M–O distances are short (*c.* 2.0 Å). (ii) The coordination geometry of M is (distorted) tetrahedral, e.g. with M = Ag^{I}. In this compound, the Pt–M–Pt angle deviates markedly from 180°, the nucleobases are substantially (64–78°) tilted with respect to the Pt coordination planes, and M–O distances are much longer (2.4–2.6 Å).

The overall structure of Pt_2Tl is, although similar in some respects to Pt_2Ag (bent structure, tilting of nucleobase, long M–O bonds), nevertheless also markedly different from it and even more so from compounds (i). The dramatic difference originates from the relative orientation of the two 'halves' of the cation. If the trinuclear Pt_2M ($M = Ag^I$ or Tl^I) cations are 'divided' in two PtM entities, their geometries are similar as far as the base tilting relative to the PtN_4 plane is concerned, angles being 62.5° (rings b and ba) and 67.2° (rings a and aa). Expectedly, M–O bonds are considerably longer for $M = Tl^I$, 2.791(6) and 2.921(7) Å. The two'halves' of Pt_2Tl, which are related by a C_2 symmetry operation, are assembled in such a way that two of the four 1-MeT planes (rings b and ba), one of each 'half', are parallel and stacked on each other (distance 3.50 Å). As a consequence, a wide cleft opens at the Tl. Apart from the coordinating oxygens and the two Pts, which are at a distance of 3.085(1) Å from Tl, there are no other contacts of atoms with Tl that could be interpreted in terms of a bond. The shortest intermolecular distances of Tl are those to water oxygens, which are 3.637(8) and 3.766(8) Å, and certainly too long to be considered bonds (Fig. 2). We suggest that the Tl^I in Pt_2Tl has a stereoactive electron lone pair, formally a hybrid with s, p and possibly d contributions, which is oriented along the C_2 axis. In fact, a feature established for subvalent Group IV compounds with stereoactive lone pairs [20] applies also to our compound: the two Tl–O bonds adjacent to the lone pair (Tl–O4a and Tl–O4aa, 2.921(7) Å) are significantly (11 σ) longer than the two other Tl–O bonds (Tl–O4b and Tl–O4ba, 2.791(6) Å) which are farther away. Due to the electronegativity of Tl, the space requirement of the lone pair will not be too pronounced, explaining why the O4a–Tl–O4aa angle (140.9(3)°) is not larger. The protons of the water molecules would then be in a position to make H bonding contacts with the lone pair at the Tl.

The Pt–Tl separations within the cation are 3.085(1) Å. This distance is shorter than the 3.140(1) Å found in $Tl_2Pt(CN)_4$ [11a], comparable to the 3.034(1)–3.047(1) Å distances in a tetrahedral Pt_3Tl cluster [21], but longer than in a PtTl compound (2.911(2) Å [11b]), where the Tl is linked to the Pt via a bridging ligand. In all three cases, the Pt–Tl contacts are considered metal–metal bonds. It therefore appears appropriate to also describe the Pt–Tl contacts in our compound as metal–metal bonds and to ascribe Tl a coordination number of six. An alternative description – a PtTlPt triangle with two Pt–Tl bonds and without any marked Tl–O bonding – seems less valid. Even though Pt is somewhat out of its coordination plane (0.030 Å) and directed toward the Tl, Tl would be two-coordinate only in that case. A similar arrangement, as far as metals are concerned, is found in $[Ir_2(CO)Cl]_2Tl(\mu\text{-}L)_2$ (L = bridging diphosphine) [10b, 22] (Ir–Tl–Ir, 139.4°; Pt–Tl–Pt, 136.7(1)°), but there Tl forms two additional bonds to a nitrate. As outlined above, this is not the case in our compound, however.

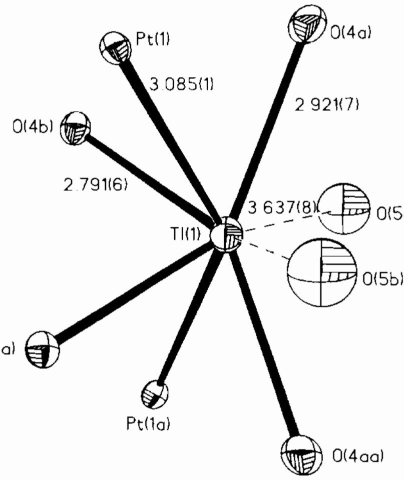

Fig. 2. Coordination geometry of Tl. It can be described as a distorted trigonal antiprism (solid lines) with the trigonal pyramids (Tl1, O4b, Pt1, O4a) tilted away from the C_2 axis due to the lone pair.

The 1-MeT rings do not display any unusual structural features. Geometries compare well with 1-MeT rings in Pt_2Ag [16]. As in most complexes of N3 metalated 1-methylthymine, the differentiation between N1 and C5 as well as O2 and O4 is not fully straightforward due to the pseudo C_2 symmetry axis through N3 and C6. However, from comparison with a series of similar 1-methyluracil complexes it appears safe to assume that O4 is more basic than O2 and therefore Tl is also coordinated via O4 oxygens rather than O2 oxygens.

Figure 3 gives a stereoview of the unit cell along the *c* axis. Cations are arranged in such a way that in addition to intramolecular base stacking between rings b and ba, which is roughly along the *a* axis, there is also intermolecular stacking between thymine rings a and aa along the *c* axis. Strands of cations extend throughout the *ac* plane with nitrates in between, while H bonding interactions between the cation planes are established by water molecules. None of these H bonding interactions are unusual.

^1H NMR spectra of *cis*-$[(NH_3)_2PtL_2TlL_2Pt(NH_3)_2]^+$ (L = 1-MeT or 1-MeU) or of mixtures of *cis*-$(NH_3)_2PtL_2$ and $TlNO_3$ in D_2O, give rise to single, averaged signal sets of the nucleobases, which are shifted downfield relative to *cis*-$(NH_3)_2PtL_2$. This behavior indicates rapid exchange between bound and free Tl.

Tl^I binding to *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2$ has a minor effect in its IR and Raman (solid state) spectra. Except for the additional bands due to NO_3^- (IR: 1380 cm^{-1}; Raman: 1052 cm^{-1}), neither relative intensities of bands nor their positions are affected strongly. In fact, Raman and IR spectra of $PtTl_2$ and Pt_2Ag are very similar, suggesting essentially ionic interactions between exocyclic oxygens and the metal, as previously outlined for Pt_2Ag [16]. See 'Supplementary material'.

Unlike $Tl_2[Pt(CN)_4]$, which was prepared and studied for comparison, the title compound does not display

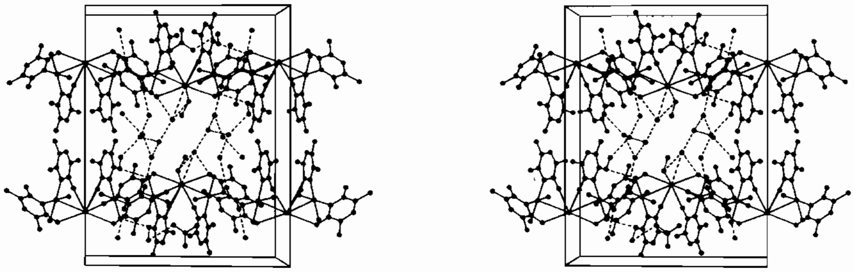

Fig. 3. Stereoview of the unit cell of the title compound along the *c* axis with H bonding interactions indicated.

any detectable luminescence when irradiated with UV light ($\lambda = 366$ nm).

Conclusions

The here described complex represents the first example of a third structural type of complex of general composition *cis*-$[(NH_3)_2PtL_2ML_2Pt(NH_3)_2]^{n+}$ (L = 1-MeT or 1-MeU). The salient feature of Pt_2Tl is the intracomplex stacking of two 1-MeT nucleobases which appears to be related to the lone electron pair at the heterometal M.

Supplementary material

Anisotropic temperature factors of the title compound, H atom coordinates and isotropic displacement coefficients, observed and calculated structure factors, a detailed structure determination summary, and Raman spectra (100–1800 cm^{-1}) for Pt_2Tl, Pt_2Ag and *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2$, can be obtained from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, under CSD 56940 on request. Requests should be accompained by the complete literature citation.

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