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Co-existing pseudo-planar and saddle conformers of tetramethyl tetraaza[14]annulene platinum complexes: X-ray crystallographic studies on [Pt^{II}(tmtaa)] and *trans*-[Pt^{IV}Cl$_2$(tmtaa)] †

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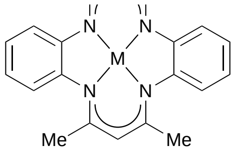
Orange platelets of [Pt(tmtaa)], where H$_2$tmtaa = 6,8,15,17-tetramethyl-5,6,9,14,15,18-hexahydrodibenzo[*b*,*i*][l,4,8,11]-tetraazacyclotetradecine, show the expected 'pseudo-planar' centrosymmetric macrocyclic conformation but red needles of another [Pt(tmtaa)] modification and purple *trans*-[PtCl$_2$-(tmtaa)] both show saddle-form co-ordination with the metal ion only 0.046(1) Å (Pt^{2+}) or 0.024(5) Å (Pt^{4+}) above the N$_4$ plane; X-ray powder diffraction reveals similar dimorphism for [Pd(tmtaa)] but not for [Ni(tmtaa)].

The [M(tmtaa)] complexes are the most familiar members of a widely studied class of tetraaza[14]annulene chromophores which resemble metalloporphyrins in significant respects.[1–6] Steric congestion between each methyl group and the adjacent C–H of the neighbouring benzo moiety induces pronounced saddle-shaped ruffling, the usual hallmark of the metallated tmtaa^{2-} macrocycle. The saddle form (with β-diiminato planes folded down, benzo-α-diimine planes folded up) tends to tilt the C=N–C donor groups, so that the metal lies above the N$_4$ plane in accord with the marked propensity for pyramidal co-ordination[7] and M–M linked dimerisation.[8]



[Mtmtaa]

In sharp contrast, the early report[9] of 'pseudo-planar' [Pd-(tmtaa)] revealed centrosymmetric molecular geometry, with the metal exactly located in the donor plane and with distinctly shallower, necessarily chair-like macrocycle folding (described below). This has led to long-standing acceptance of a structural dichotomy,[9–11] on the assumption that [Ni(tmtaa)] adopts the saddle form while enhanced ligand-field effects dictate strictly planar co-ordination for the heavier Pd and Pt d^8 ions. However, X-ray measurements ‡ on a red needle of [Pt(tmtaa)] isolated in our laboratory revealed a different unit cell § and the classical saddle-form molecular conformation, **I**, Fig. 1. Powder diffraction checks on batches of [Pt(tmtaa)] showed only small quantities of **I** (⩽10%) together with a more abundant modification matching the literature description of [Pd(tmtaa)]. Single-crystal studies ‡ on a representative orange platelet have established the detailed structure of the Pt-containing pseudo-planar form **II**.

Fig. 2 compares X-ray powder diffraction patterns for the analytically pure materials [M(tmtaa)] (M = Cu, Pd or Pt). The Pd complex is most obviously dimorphic, generally containing roughly equal amounts of the $P2_1/n$ form[9] and a previously unnoticed modification isomorphous with the structurally determined[11] ($P2_1/c$) saddle-form [Cu(tmtaa)]. For Ni, only a single component is detected, also crystallographically isomorphous with [Cu(tmtaa)]. Thus, contrary to earlier belief, *all three* d^8 species can achieve the saddle-form conformation. The characteristic displacement of the M^{II} ion above the rectangular N$_4$ plane is reduced to 0.042(1) (Ni), 0.060(1) (Pd) and 0.046(1) Å for Pt,[6] in comparison with 0.070 (Cu), 0.114 (Fe) and 0.50 Å for binuclear Cr.[1]

This work was prompted by our interest in the capacity of certain simple Pt^{II}L$_4$ species to function as precursors to unsupported metal–metal-bonded Pt^{III} dimers of the form [Cl–(PtL$_4$)–(PtL$_4$)–Cl],[13] recently established for both [Pt(α-dioxime)$_2$] and [Pt(β-diketonate)$_2$].[14,15] Despite the stability of the [M(tmtaa)–M(tmtaa)] architecture in other contexts (M^{II} = Cr, Mo, Ru or Rh),[8] treatment of [Pt(tmtaa)] with Cl$_2$ led to preferential separation of purple needles of *trans*-[PtCl$_2$(tmtaa)] suitable for single-crystal X-ray analysis.‡ Three

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† *Supplementary data available* (No. SUP 57313, 2 pp.): technical data on GAUSSIAN 94 calculations. See *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

‡ CCDC reference number 186/729.

	[Pt(tmtaa)] **I**, saddle	[Pt(tmtaa)] **II**, chair	[PtCl$_2$(tmtaa)] **III**, saddle
Formula	C$_{22}$H$_{22}$N$_4$Pt	C$_{22}$H$_{22}$N$_4$Pt	C$_{22}$H$_{22}$Cl$_2$N$_4$Pt
M	537.54	537.54	608.44
Crystal habit	Deep red needle	Orange plate	Purple needle
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/a$ (no.14)	$P2_1/n$ (no. 14)	*Pbcn* (no. 60)
a/Å	7.858(2)	6.5590(9)	14.580(1)
b/Å	19.457(2)	18.742(2)	8.284(2)
c/Å	12.294(2)	7.365(1)	16.687(2)
β/°	90.43(2)	104.75(1)	—
U/Å^3	1879.7(5)	875.5(2)	2015.5(5)
Z	4	2	4
D_c/g cm^{-3}	1.899	2.039	2.005
μ/cm^{-1}	75.5	152	150
Crystal size/mm	0.31 × 0.10 × 0.05	0.12 × 0.14 × 0.04	0.16 × 0.03 × 0.04
Diffractometer, radiation	Rigaku AFC6S, Mo-Kα	Rigaku AFC6R, Cu-Kα	Rigaku AFC6R, Cu-Kα
λ/Å	0.710 69	1.541 78	1.541 78
Unique, total reflections	3455, 3717	1364, 1488	1754, 1754
Variables	244	125	134
R_{int}	0.039	0.043	—
R, *R′*	0.026, 0.017	0.023, 0.031	0.016, 0.014
F(000)	1040	520	1176

§ The conventional unit cells adopted here for the two monoclinic modifications of [Pt(tmtaa)] transform to $P2_1/c$ (no. 14) as follows: in $P2_1/c$, the saddle form, **I**, has $a = 14.541$, $b = 19.457$, $c = 7.858$ Å, $\beta = 122.3°$, $Z = 4$, whereas the chair form, **II**, has $a = 7.365$, $b = 18.742$, $c = 8.5244$ Å, $\beta = 131.9°$, $Z = 2$. Neither can be confusd with the typical $P2_{16}/c$ unit cell of [M(tmtaa)] (M = Ni, Pd or Cu) where, *e.g.*, [Ni(tmtaa)][16] has $a = 14.506(2)$, $b = 16.457(2)$, $c = 16.102(3)$ Å, $\beta = 99.32(1)°$, $Z = 8$.

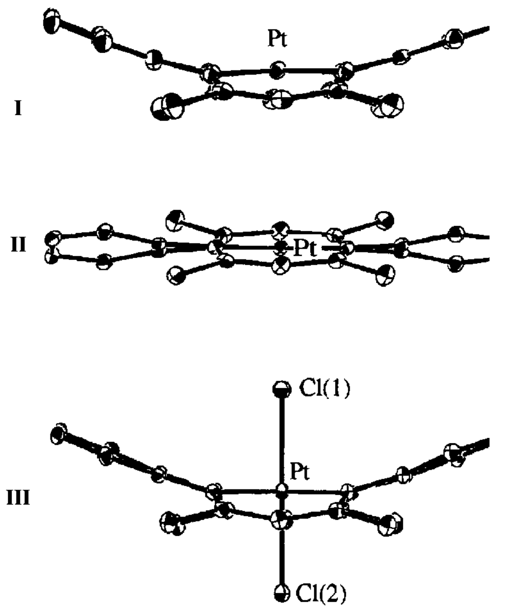

Fig. 1 Thermal ellipsoid plots[12] for tmtaa^{2-} complexes. In each case, the N_4 plane is shown exactly horizontal (*i.e.*, edgeways)

Table 1 Geometric data for platinum tetraaza[14]annulenes

Parameter[a]	[Pt(tmtaa)] **I**, saddle	[Pt(tmtaa)] **II**, chair	[PtCl$_2$(tmtaa)] **III**, saddle
α/°	132.8(7)	132.9(7)	132.7(5)
β/°	122.7(6)	122.8(7)	123.1(5)
γ/°	127.3(6)	125.2(6)	129.1(4)
δ/°	115.0(6)	115.1(6)	115.4(4)
1–2/°	(−)18.8(3)	(±)13.6(3)	(−)19.1(2)
1–3/°	(+)14.4(3)	1.5(4)[b]	(+)17.7(3)
1–4/°	20.2(9)	12.9(3)[b]	22.2(2)
Pt–N/Å	1.981(5)	1.997(6)	2.001(4)
N–Pt–N/°	97.6(2)	97.7(2)	97.7(2)
h(Pt–N_4)/Å	0.046(1)	—	0.024(5)
d(C–C)/Å	2.98(1)	2.91(1)	3.01(1)

[a] Mean dimensions (bond angles, dihedral angles and distances) as defined in Fig. 2(*a*); N–Pt–N = β-diiminato bite angle, *h* = height of Pt above N_4 plane. For averaged parameters, largest individual estimated standard deviations (e.s.d.s) are quoted. [b] Twisted, not folded, see text.

notable features of the six-co-ordinate Pt^{IV} structure, **III**, are: (*i*) retention of the ruffled form, (*ii*) minimal displacement of the metal ion, 0.024(5) Å being the smallest value yet recorded for a saddle conformation, (*iii*) parity of the Pt–Cl(1) and Pt–Cl(2) bonds [2.336(2) and 2.337(2) Å respectively] despite their physically distinct environments.

These studies clarify the general relationship between differing M–tmtaa conformations. Firstly, the saddle-form accommodates *but does not demand* marked pyramidal displacement. Indeed the metal will automatically tend to approach the N_4 plane, no matter how pronounced the ruffling, so long as the downward chelate folding at the long N···N edge is matched by the upward folding at the short edge. This is illustrated by the convergence of the dihedral angles 1–2 and 1–3, listed in Table 1.¶ The measured difference between 1–2 and 1–3 diminishes from 4.4(4)° in **I** to 1.4(4)° in **III**, as the metal approaches the N_4 plane. In the pyramidal [M(tmtaa)] structures considered previously for other metals,[11] greater disparity in folding (1–2 > 1–3) is invariably present.

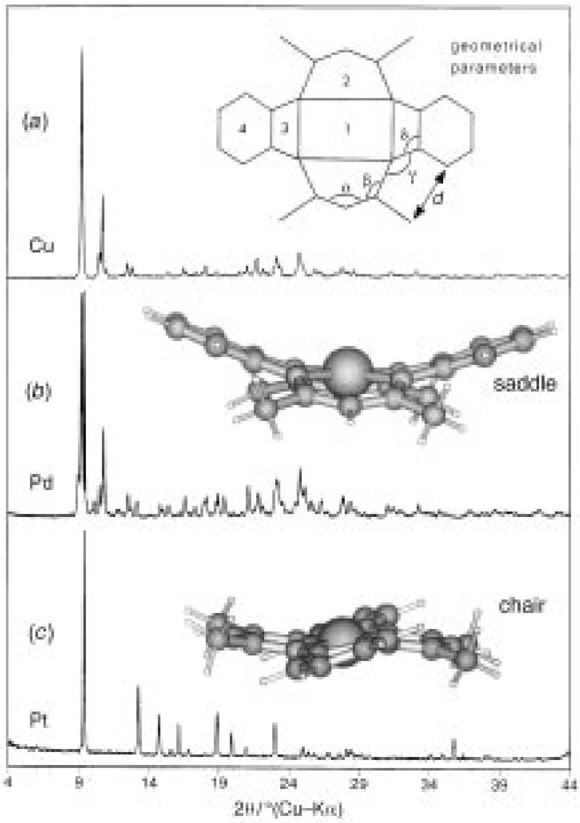

Fig. 2 Comparative X-ray powder patterns for [M(tmtaa)]; (*a*) M = Cu, (*b*) M = Pd, dimorphic material, (*c*) M = Pt, largely **I**. Upper inset[4] relates to Table 1. Lower insets show the geometry-optimised (GAUSSIAN 94) conformational minima for [Pt(tmtaa)], matching **I** and **II**; in 2(*c*), the viewpoint differs by 90° and the N_4 plane is level from left to right, attesting to twisting of plane 4

However, in centrosymmetric **II** the two β-diiminato six-membered metal–chelate rings are themselves inclined in opposite senses, by definition, and the 1–2 angle is restricted to ≈14°. Folding at the α-diimine N···N edge (1–3) is essentially zero; steric compression leads instead to obvious twisting of each fused benzene ring, visible in Fig. 1, in response to the torque applied by the two adjacent methyl groups (one lying above, one below). In this case, 1–3 folding (or simple 3–4 folding along benzo C–C) would only aggravate the clash with one methyl group as the clash with the other was relieved. Detailed comparisons with the molecular geometry of [Ni(tmtaa)] (saddle) and [Pd(tmtaa)] (saddle and chair) will be reported shortly.[16]

Optimal ligand-field stabilisation energy (LFSE) no doubt contributes to the existence of centrosymmetric **II** by off-setting the energetic cost of distorting the benzo groups. However, LFSE effects also favour the exceptionally close approach of the d^8 (or d^6) ions to the N_4 plane in the ruffled conformations, **I** and **III** described above. Remarkably enough, preliminary *ab initio* calculations|| also predict two distinct conformational minima corresponding to **I** and **II**, as depicted in Fig. 2, and capture the buckling distortion of **II**.

Solutions of [Pd(tmtaa)] and [Pt(tmtaa)] are spectroscopically invariant, with only one species detected between 200 and 300 K regardless of the polymorphic ratio of the source material. Further NMR spectroscopic studies, exploiting the Nuclear Overhauser Effect, show the prevailing conformation of [Pt(tmtaa)] in CH_2Cl_2 at 300 K to be largely or exclusively

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¶ These folds refer to the dihedral angles between the planes defined in Fig. 2(*a*) (inset), following ref. 4. In saddle-form complexes, the 1–3 fold is complemented by a further 3–4 fold of *ca.* 5° at the benzo C–C fusion.

|| By geometry-optimisation (GAUSSIAN 94), two conformational minima were found in each case, with **I** favoured over **II** in the gas-phase by 34.4 kJ mol^{-1} for M = Pd, and by 30.7 kJ mol^{-1} for M = Pt; GAUSSIAN 94 (revision D3) software supplied by Gaussian Inc., Carnegie Office Park, Pittsburgh, PA.

II.[17] Interestingly, a second crystalline form has been recorded for [Ni(tmtaa)],[18] however, this structure (with $P2_1/n$ unit-cell dimensions incommensurate with those reported here) also embodies saddle-form co-ordination.

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