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Platinum(II) Complexes of Methyl-substituted Xanthines: Crystal Structures of K[Pt(theobromine)Cl_3]·H_2O, *trans*-[Pt(isocaffeine)$_2Cl_2$]·H_2O and K(isocaffeinium)[$PtCl_4$]·H_2O

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Abstract

The preparations of Pt(theophylline)$_2Cl_2$, K[Pt(theophylline)Cl_3], K[Pt(theobromine)Cl_3]·H_2O (**1**), *trans*-[Pt(isocaffeine)$_2Cl_2$]·H_2O (**2**), and K(isocaffeinium)[$PtCl_4$]·H_2O (**3**) are reported.

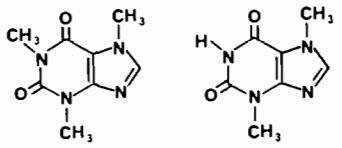
Crystals of **1** are monoclinic $P2_1/n$ with a = 7.641(2), b = 11.873(3), c = 15.868(4) Å, β = 90.80(2)°, Z = 4. The structure was refined on 1443 reflections to R = 0.028. In the planar [Pt(theobromine)Cl_3]$^-$ anion Pt–N(9) = 2.016(6) Å, Pt–Cl = 2.299(2), 2.289(2), and 2.303(2) Å. The imidazole ring is rotated away from the coordination plane by 79.8°. Symmetry related theobromine units pack parallel to each other with a mean inter-ring separation of 3.27 Å.

Crystals of **2** are monoclinic $P2_1/a$ with a = 7.345(2), b = 20.021(5), c = 8.031(2) Å, β = 104.18(2)°, Z = 2. The structure was refined on 1132 reflections to R = 0.029. The Pt–N(7) distance is 2.003(3) Å and Pt–Cl = 2.298(1) Å. The imidazole ring is rotated away from the $PtCl_2N_2$ plane by 76.8°. In this compound, the isocaffeine units do not stack, but form a staggered arrangement within the unit cell.

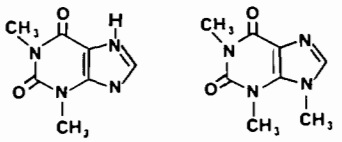
Crystals of **3** are monoclinic $P2_1/c$ with a = 7.382(1), b = 14.014(4), c = 15.757(4) Å, β = 92.30(2)°, Z = 4. The structure was refined on 2057 reflections to R = 0.032. The isocaffeine is protonated at N(7). The Pt–Cl distances in the $PtCl_4^{2-}$ anion range between 2.29–2.31 Å. The protonated isocaffeine cations and the $PtCl_4^{2-}$ anions form a very nearly parallel infinitely stacked arrangement with minimum interlayer atomic separations of 3.37 and 3.44 Å.

Introduction

The methyl-substituted xanthines, caffeine (**I**), theobromine (**II**) and theophylline (**III**) are important components of a range of beverages (coffee, tea, cocoa, and chocolate products) and medicinals. Their pharmacological properties are a matter of continuing investigation and interest [1, 2]. They are also



I **II**



III **IV**

relevant to cancer therapy because of their ability to sensitize cells towards the cytotoxic effects of UV radiation, alkylating agents [3] and *cis*-Pt$(NH_3)_2Cl_2$ [4, 5]. Because of this, and the continuing search for analogues of *cis*-Pt$(NH_3)_2Cl_2$ with more favourable anti-cancer activity, there has been interest in the platinum complexes of **I**–**III**, and related ligands such as isocaffeine (**IV**).

Griffith and Amma [6] showed that theophylline binds to platinum via N(9) in the compound (theophyllinium)[Pt(theophylline)Cl_3]. Cramer and his co-workers [7] found that K[Pt(caffeine)Cl_3] has anti-cancer activity and they also reported the results of an X-ray study on ($MePh_3P$)[Pt(caffeine)Cl_3]. Bushnell *et al.* have described the structures of *cis*-[Pt(isocaffeine)$_2$(PEt_3)$_2$](BF_4)$_2$ and *cis*-[PtCl(caffeine)(PEt_3)$_2$]BF_4 and they also obtained the theophylline and isocaffeine analogues of the latter compound [8]. The structures of [Pten(isocaffeine)$_2$](PF_6)$_2$ [9], its nitrate analogue (as a dihydrate) [9], and *cis*-[Pt(caffeine)$_2Cl_2$]·0.4H_2O (**4**) [10] have also been reported. Other caffeine complexes of the type [Pt(caffeine)(nucleoside)Cl_2] have been described [10, 11] but not structurally characterized by X-ray methods.

During studies [12] aimed at extending the range of platinum complexes formed by ligands **I**–**IV**, we

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TABLE I. Summary of Crystal Data and Intensity Collection

Compound	1	2	3
Formula	$C_7H_{10}N_4O_3Cl_3KPt$	$C_{16}H_{22}N_8O_5Cl_2Pt$	$C_8H_{13}N_4O_3Cl_4KPt$
M_r	538.8	672.4	589.2
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/a$	$P2_1/c$
a (Å)	7.641(2)	7.345(2)	7.382(1)
b (Å)	11.873(3)	20.021(5)	14.014(4)
c (Å)	15.868(4)	8.031(2)	15.757(4)
β (°)	90.80(2)	104.18(2)	92.30(2)
Cell volume (Å^3)	1439	1145	1629
Molecules/unit cell	4	2	4
ρ (calc.) (g cm^{-3})	2.49	1.95	2.40
μ (calc.) (cm^{-1})	265	141	250
Radiation	Cu Kα	Cu Kα	Cu Kα
Crystal dimensions (mm)	0.2 × 0.2 × 0.2	0.3 × 0.5 × 0.2	0.15 × 0.1 × 0.2
Unique reflections measured	1699	1173	2488
2θ range (°)	100	100	116
Reflections considered observed $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	1443	1132	2057
Weight (G)[a]	0.00007	0.00028	0.00028
No. of parameters varied	183	196	212
R	0.028	0.029	0.032
R_w	0.029	0.032	0.033
Absorption correction	numerical	empirical	numerical

[a] $w^{-1} = \sigma^2(F) + GF^2$.

have determined by X-ray diffraction methods the structures of the new compounds K[Pt(theobromine)Cl_3]·H_2O and *trans*-[Pt(isocaffeine)$_2Cl_2$]·H_2O. We report here the results of this work and also the structure of K(isocaffeinium)[$PtCl_4$]·H_2O, which resulted from an attempt to prepare crystals of K[Pt(isocaffeine)Cl_3].

Experimental

Preparations

Pt(theophylline)$_2Cl_2$ and trans-[Pt(isocaffeine)$_2$-Cl_2]·H_2O

These were prepared by the method previously reported [10] for *cis*-Pt(caffeine)$_2Cl_2$. The theophylline complex was yellow and was obtained in 72% yield: *Anal.* Found: C, 27.21; H, 2.96; N, 17.51. Calc. for Pt(theophylline)$_2Cl_2$: C, 26.84; H, 2.57; N, 17.89%. IR, ν(Pt–Cl) 330, 325 sh cm^{-1}.

The isocaffeine complex was obtained as yellow crystals, but in very low yield (6%) and was characterized by single crystal X-ray diffraction study. IR, ν(Pt–Cl) 335 cm^{-1}.

K[Pt(theophylline)Cl_3] and K[Pt(theobromine)-Cl_3]·H_2O

These were obtained by the method described [10] for K[Pt(caffeine)Cl_3] employing the more direct (organic solvent) route.

Theophylline complex: methanol used as solvent, orange–yellow product (41% yield). *Anal.* Found: C, 15.82; H, 1.63; N, 10.46. Calc. for K[Pt(theophylline)Cl_3]: C, 16.14; H, 1.55; N, 10.75%. IR, ν(Pt–Cl) 341sh, 330 cm^{-1}.

Theobromine complex: acetone solvent, orange crystals (52% yield). *Anal.* Found: C, 16.15; H, 1.84; N, 10.60. Calc. for K[Pt(theobromine)Cl_3]·H_2O: C, 15.61; H, 1.87; N, 10.40%. IR, ν(Pt–Cl) 340, 323 cm^{-1}.

K(isocaffeinium)[$PtCl_4$]·H_2O

Red crystals (29% yield) were obtained from an attempt to prepare K[Pt(isocaffeine)Cl_3] by the method [10] for K[Pt(caffeine)Cl_3] in acetone. *Anal.* Found: C, 16.39; H, 2.13; N, 9.26. Calc. for K(isocaffeinium)[$PtCl_4$]·H_2O: C, 16.31; H, 2.22; N, 9.51%. IR, ν(Pt–Cl) 318 cm^{-1}.

X-ray Studies

A summary of the crystal data and of the data collection and refinement parameters for the compounds K[Pt(theobromine)Cl_3]·H_2O (**1**), *trans*-[Pt(isocaffeine)$_2Cl_2$]·H_2O (**2**), and K(isocaffeinium)[$PtCl_4$]·H_2O (**3**) is given in Table I. Intensity data were measured with graphite monochromated Cu Kα radiation using ω-scans on a Nicolet R3m/Eclipse S140 diffractometer system. The data were corrected for Lorentz and polarization factors.

All three structures were solved by the heavy-atom method and their non-hydrogen atoms were refined

TABLE II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for 1

Atom	x	y	z	U^a
Pt	333(1)	1318(1)	3995(1)	25(1)
Cl(1)	2986(3)	582(2)	4417(1)	42(1)
Cl(2)	177(3)	97(2)	2881(1)	40(1)
Cl(3)	−2367(3)	2026(2)	3609(2)	50(1)
K	3651(3)	515(2)	6403(1)	41(1)
N(1)	2174(8)	5370(5)	5764(4)	30(2)
C(2)	2734(9)	5074(6)	4981(5)	25(3)
O(2)	3612(7)	5709(4)	4555(4)	39(2)
N(3)	2230(7)	4020(5)	4693(4)	26(2)
C(3)	2880(11)	3614(7)	3893(5)	34(3)
C(4)	1124(9)	3367(6)	5187(5)	25(3)
C(5)	619(10)	3731(6)	5953(5)	24(3)
C(6)	1121(10)	4780(6)	6320(5)	27(3)
O(6)	690(7)	5180(5)	6991(4)	41(2)
N(7)	−444(7)	2901(5)	6270(4)	25(2)
C(7)	−1278(11)	2882(7)	7093(5)	38(3)
C(8)	−558(10)	2102(7)	5687(5)	32(3)
N(9)	387(7)	2362(5)	4997(4)	23(2)
Oh	9465(9)	2284(6)	1485(5)	68(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for **2**

Atom	x	y	z	U^a
Pt	0	0	0	31(1)
Cl	2192(2)	794(1)	−212(2)	50(1)
N(1)	4205(6)	−1920(2)	1860(5)	37(2)
C(1)	4685(9)	−2419(3)	685(8)	54(3)
C(2)	4950(9)	−2038(3)	3600(9)	41(2)
O(2)	5860(5)	−2541(2)	4105(5)	51(1)
N(3)	4560(7)	−1573(3)	4730(6)	38(2)
C(3)	5217(12)	−1709(4)	6584(8)	67(3)
C(4)	3499(7)	−1031(2)	4085(6)	32(2)
C(5)	2701(7)	−946(2)	2377(6)	31(2)
C(6)	3043(7)	−1401(3)	1113(7)	34(2)
O(6)	2425(5)	−1363(2)	−423(4)	43(1)
N(7)	1698(5)	−354(2)	2163(5)	33(2)
C(8)	1914(11)	−105(3)	3699(11)	37(2)
N(9)	3018(6)	−490(2)	4920(5)	33(1)
C(9)	3429(9)	−311(3)	6762(7)	45(2)
O(1a)	1143(14)	1211(4)	5735(12)	61(4)
O(1b)	296(15)	1356(5)	3894(15)	77(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

anisotropically. The positions of the water molecules and of all the hydrogen atoms, with the exception of those of the water molecule in structure **1** were located from ΔF maps. In **2** two 0.5 occupancy positions were found for the water molecule. In each case

TABLE IV. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for **3**

Atom	x	y	z	U^a
Pt	1717(1)	2296(1)	4052(1)	32(1)
K	2616(2)	1488(1)	1561(1)	44(1)
Cl(1)	359(3)	2839(1)	2796(1)	44(1)
Cl(2)	3058(3)	1749(1)	5305(1)	49(1)
Cl(3)	1470(3)	3792(1)	4632(1)	48(1)
Cl(4)	1974(3)	796(1)	3494(1)	53(1)
N(1)	5584(8)	1515(4)	−1835(3)	38(2)
C(1)	4783(12)	1035(7)	−2588(5)	55(3)
C(2)	5923(10)	2483(5)	−1901(5)	39(2)
O(2)	5607(8)	2904(4)	−2554(3)	52(2)
C(3)	6946(12)	3965(6)	−1244(6)	55(3)
N(3)	6619(8)	2949(4)	−1174(4)	34(2)
C(4)	6944(9)	2417(5)	−461(4)	33(2)
C(5)	6587(10)	1478(5)	−422(4)	34(2)
C(6)	5861(10)	945(5)	−1121(5)	40(2)
O(6)	5525(8)	93(3)	−1120(3)	52(2)
N(7)	7065(9)	1183(4)	390(4)	45(2)
C(8)	7680(11)	1921(6)	818(5)	45(3)
C(9)	8202(12)	3639(6)	643(5)	52(3)
N(9)	7627(8)	2700(4)	318(4)	40(2)
O(10)	9549(10)	330(5)	1812(4)	76(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

the NH and, where located, the OH hydrogen atoms were refined isotropically. All the other hydrogen atom positions were idealised, C–H = 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2\ U_{eq}(C)$, and allowed to ride on their parent carbons. The orientations of the methyl groups were determined from ΔF maps and the groups refined as rigid bodies. Refinements were by block-cascade full-matrix least-squares. Computations were carried out using the SHELXTL programme system [13]. Fractional coordinates for the non-hydrogen atoms in **1**, **2**, and **3** are given in Tables II, III, and IV respectively. Tables V–VII give the bond lengths and angles, with the exception in each case of selected values for the purine nuclei, which are grouped in Table VIII.

Discussion

Our attempts to add to the known complexes [6, 7, 10] of types PtL_2Cl_2 and $PtLCl_3^-$ formed by **I**–**IV** met with limited success in the formation of Pt(theophylline)$_2$Cl$_2$, Pt(isocaffeine)$_2$Cl$_2$·H$_2$O, and K[Pt(theobromine)Cl$_3$]·H$_2$O. The potassium salt analogue of (theophyllinium)[Pt(theophylline)Cl$_3$] [6] was also obtained. Attempts to prepare K[Pt(isocaffeine)Cl$_3$] using the procedure successfully employed [10] for K[Pt(caffeine)Cl$_3$] resulted in the formation of K(isocaffeinium)[PtCl$_4$]H$_2$O.

TABLE V. Bond Lengths (Å) and Angles (°) for **1** (see also Table VIII)

Pt–Cl(1)	2.299(2)	Pt–Cl(2)	2.289(2)
Pt–Cl(3)	2.303(2)	Pt–N(9)	2.016(6)
C(2)–O(2)	1.220(9)	C(6)–O(6)	1.216(10)
N(3)–C(3)	1.451(11)	N(7)–C(7)	1.462(10)
Cl(1)–Pt–Cl(2)	91.2(1)	Cl(1)–Pt–Cl(3)	178.2(1)
Cl(2)–Pt–Cl(3)	89.4(1)	Cl(1)–Pt–N(9)	89.7(2)
Cl(2)–Pt–N(9)	177.7(2)	Cl(3)–Pt–N(9)	89.7(2)
N(1)–C(2)–O(2)	121.8(7)	C(2)–N(3)–C(3)	119.5(6)
O(2)–C(2)–N(3)	121.9(7)	C(3)–N(3)–C(4)	121.6(6)
N(1)–C(6)–O(6)	121.7(7)	C(5)–C(6)–O(6)	128.6(7)
C(7)–N(7)–C(8)	125.9(7)	Pt–N(9)–C(8)	119.4(5)

TABLE VI. Bond Lengths (Å) and Angles (°) for **2** (see also Table VIII)

Pt–Cl	2.298(1)	C(2)–O(2)	1.221(7)
Pt–N(7)	2.003(3)	N(3)–C(3)	1.474(8)
N(9)–C(9)	1.479(7)	C(6)–O(6)	1.208(6)
Cl–Pt–N(7)	90.6(1)	N(1)–C(6)–O(6)	121.7(5)
N(7)–Pt–Cl′	89.4(1)	C(8)–N(9)–C(9)	121.9(5)
N(7)–Pt–N(7′)	180.0	C(1)–N(1)–C(6)	116.7(4)
Cl–Pt–Cl′	180.0	N(1)–C(2)–O(2)	121.5(6)
C(1)–N(1)–C(2)	115.5(5)	O(2)–C(2)–N(3)	121.6(6)
C(2)–N(3)–C(3)	118.1(5)	Pt–N(7)–C(8)	126.3(4)

TABLE VII. Bond Lengths (Å) and Angles (°) for **3** (see also Table VIII)

Pt–Cl(1)	2.312(2)	C(9)–N(9)	1.468(10)
Pt–Cl(2)	2.303(2)	C(2)–O(2)	1.200(9)
Pt–Cl(3)	2.297(2)	C(3)–N(3)	1.449(10)
Pt–Cl(4)	2.290(2)	C(6)–O(6)	1.219(9)
N(1)–C(1)	1.468(10)		
Cl(1)–Pt–Cl(2)	179.7(1)	C(1)–N(1)–C(6)	115.6(6)
Cl(1)–Pt–Cl(3)	90.1(1)	N(1)–C(2)–O(2)	121.1(7)
Cl(1)–Pt–Cl(4)	90.7(1)	O(2)–C(2)–N(3)	121.7(7)
Cl(2)–Pt–Cl(3)	90.1(1)	C(2)–N(3)–C(3)	116.9(6)
Cl(2)–Pt–Cl(4)	89.1(1)	N(1)–C(6)–O(6)	122.8(7)
Cl(3)–Pt–Cl(4)	179.2(1)	C(8)–N(9)–C(9)	121.5(6)
C(1)–N(1)–C(2)	117.1(6)		

Compound **1**, which, to our knowledge, is the first complex containing theobromine coordinated to a metal atom to be structurally characterized, consists of discrete K^+ ions, $[Pt(theobromine)Cl_3]^-$ anions and water molecules of crystallisation. The geometry within the anion (Fig. 1) involves square planar coordination about Pt (all angles within 1.2° of 90°, Table V).

The Pt-donor atom bond lengths (Pt–N(9) 2.016(6), Pt–Cl 2.299(2), 2.289(2), and 2.303(2) Å) are, within statistical significance, the same as those found in $[Pt(caffeine)Cl_3]^-$ [7] and in $[Pt(theophylline)Cl_3]^-$ [6]. In each case the shortest Pt–Cl bond is that *trans* to the Pt–N bond.

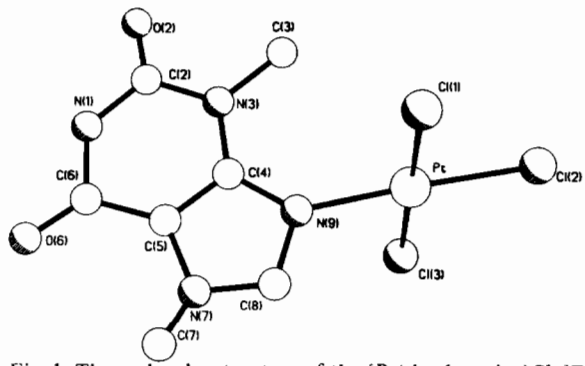
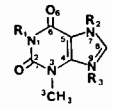


Fig. 1. The molecular structure of the $[Pt(theobromine)Cl_3]^-$ anion, giving the crystallographic numbering scheme.

TABLE VIII. Comparisons of the Bond Lengths and Angles for the Purine Nucleus in a Range of Differently Substituted Compounds 

	1 R_1 = H, R_2 = Me, R_3 = Pt	2 R_1 = R_3 = Me, R_2 = Pt	3 R_1 = R_3 = Me, R_2 = H	4 R_1 = R_2 = Me, R_3 = Pt	5 R_1 = R_2 = Me, R_3 = H	6 R_1 = R_3 = Me, R_2-
Bond						
N(1)–C(2)	1.365(10)	1.391(8)	1.385(10)	1.397(10)	1.396(4)	1.389(2)
C(2)–N(3)	1.386(9)	1.378(9)	1.399(9)	1.379(9)	1.376(4)	1.382(2)
N(3)–C(4)	1.396(10)	1.362(7)	1.361(9)	1.375(8)	1.351(4)	1.374(2)
C(4)–C(5)	1.352(11)	1.364(7)	1.345(10)	1.343(9)	1.360(4)	1.366(2)
C(5)–C(6)	1.425(10)	1.430(8)	1.419(10)	1.435(10)	1.431(5)	1.417(2)
C(6)–N(1)	1.391(10)	1.385(6)	1.387(9)	1.381(10)	1.407(4)	1.408(2)
C(4)–N(9)	1.351(9)	1.350(8)	1.367(9)	1.353(8)	1.369(4)	1.365(2)
C(5)–N(7)	1.376(9)	1.385(6)	1.377(9)	1.384(9)	1.392(4)	1.384(2)
N(7)–C(8)	1.327(10)	1.303(9)	1.306(10)	1.322(9)	1.327(4)	1.299(2)
C(8)–N(9)	1.355(10)	1.350(8)	1.346(10)	1.344(9)	1.343(4)	1.376(2)
Angle						
C(6)N(1)C(2)	129.7(6)	127.7(5)	127.2(6)	126.8(6)	127.0(3)	126.2(1)
N(1)C(2)N(3)	116.3(6)	116.9(5)	117.1(6)	117.1(7)	117.2(3)	117.6(1)
C(2)N(3)C(4)	119.0(6)	118.7(5)	117.9(6)	119.5(6)	118.6(3)	118.4(1)
N(3)C(4)C(5)	120.7(7)	123.1(5)	123.1(6)	120.5(6)	123.8(3)	123.5(1)
C(4)C(5)C(6)	124.6(7)	121.9(4)	123.2(6)	124.5(6)	122.3(3)	121.4(1)
C(5)C(6)N(1)	109.6(7)	111.5(4)	111.4(6)	111.0(6)	111.0(3)	112.9(1)
C(4)C(5)N(7)	106.0(6)	108.4(4)	107.0(6)	105.5(6)	106.8(3)	110.7(1)
C(5)N(7)C(8)	106.9(6)	105.8(4)	108.2(6)	106.5(6)	107.9(3)	103.7(1)
N(7)C(8)N(9)	111.7(7)	112.5(5)	109.9(6)	112.5(6)	109.6(3)	114.0(1)
C(8)N(9)C(4)	104.3(6)	106.1(5)	106.9(6)	103.6(5)	107.8(3)	105.0(1)
C(5)C(4)N(9)	111.0(7)	107.3(4)	108.0(6)	111.8(6)	107.9(3)	106.6(1)
C(3)N(3)C(4)	121.6(6)	123.1(5)	125.2(6)	124.5(6)	121.9(3)	124.1(1)
C(4)N(9)R_3	136.2(5)	132.0(4)	131.6(6)	134.2(4)	124(2)	131.9(1)
C(5)C(6)O(6)	128.6(7)	126.8(5)	125.7(7)	126.1(7)	126.7(3)	126.9(1)
C(5)N(7)R_2	127.2(6)	127.6(3)	124(6)	128.0(6)	125.8(3)	–
N(3)C(4)N(9)	128.3(7)	129.7(4)	128.9(6)	127.7(6)	128.4(3)	129.9(1)
C(6)C(5)N(7)	129.3(7)	129.6(4)	129.7(6)	129.7(6)	131.0(3)	128.0(1)

TABLE IX. Deviations from Least Squares Planes (Å) and Dihedral Angle (°)

	1	2	3
Least squares planes[a]			
Imidazole	0.009(C4)	0.008(N9)	0.002(C4)
Pyrimidine: (a)	0.020(N3)	0.027(C4)	0.008(N3)
(b)	0.006(C5)	0.011(C2)	0.003(N1)
PtX_4 less Pt	0.037(Pt)	0	0.005(Pt)
Dihedral angle (°) between			
Imidazole/PtX_4	79.8	76.8	–
Imidazole/Pyrimidine: (a)	2.2	3.3	0.3
(b)	0.5	0.7	0.2

[a]Atom with maximum deviation given in parenthesis. (a) Including all pyrimidine ring atoms. (b) With major deviating atom removed.

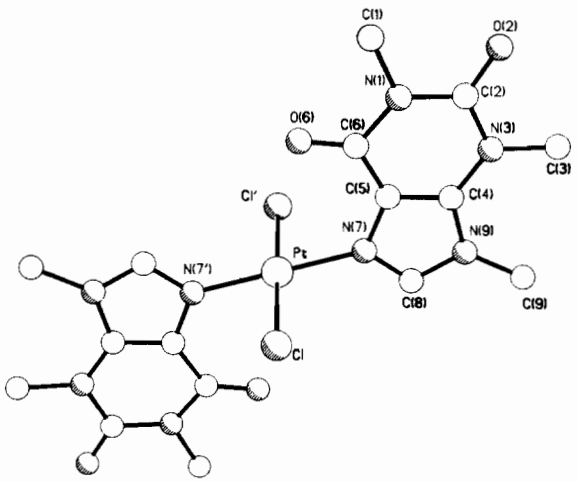


Fig. 2. Centrosymmetric *trans*-[Pt(isocaffeine)$_2$Cl$_2$] with the crystallographic numbering scheme.

The X-ray study of **2** reveals a *trans*-geometry (Fig. 2) in contrast to the situation with caffeine where, under generally similar experimental conditions, the *cis*-compound was obtained [10]. This may simply reflect the fact that, in many cases, the factors influencing the formation of *cis*- or *trans*-arrangements are finely balanced, and the adjustment of the experimental conditions to give crystals of sufficient quality for X-ray diffraction work may be crucial in deciding which geometry is adopted. (An example of the effects of experimental conditions on *cis-trans* isomerisation in PtL_2X_2 compounds is afforded by ref. 14).

In **2** the Pt–N distance (2.003(3) Å) is noticeably shorter than that (2.029(5) Å) found [10] for *cis*-Pt(caffeine)$_2$Cl$_2$, but the Pt–Cl distance is longer (2.298(1) Å compared with 2.271(2) Å in the caffeine complex). We do not attribute these differences to the change in the organic ligand but rather to the change between *cis* and *trans*-geometry, as very similar bond differences have been reported [14] for *cis*- and *trans*-dichloro-bis[1-(2-hydroxyethyl)-2-methyl-5-nitroimidazole]platinum(II).

Compound **3**, which resulted from an attempt to prepare K[Pt(isocaffeine)Cl$_3$], consists of isocaffeinium cations (protonated at N(7)) which, together with K^+ ions, act as counter ions to the $PtCl_4^{2-}$ anions.

Comparisons of the Molecular Geometries

Table IX summarizes the details of the planes of the imidazole and pyrimidine rings and the coordination spheres for all three compounds. At a first glance, the imidazole rings in all three structures are noticeably closer to planar than are the pyrimidines. However, this disparity can be seen, in each case, to be due principally to just one atom in the pyrimidine ring [N(3) in **1**, C(4) in **2**, and N(3) in **3**]. On making the same comparison, but omitting this atom, the overall planarities of the two rings are essentially the same.

Some emphasis is given in the literature to the presence of a non-zero dihedral angle between the imidazole and pyrimidine rings in purines. Table IX reveals that in structures **1**–**3** this angle is very dependent upon whether one considers the pyrimidine ring as a whole or, as we have illustrated, with the major deviant atom removed.

In both **1** and **2** there is a nearly orthogonal relationship between the plane of the imidazole ring and that of the Pt coordination sphere.

Comparison of the bond distances in both the imidazole and pyrimidine rings in **1**, **2**, and **3** with those reported in the literature [10, 15, 16] for related compounds [(caffeineH^+)$Cl^-\cdot 2H_2O$ (**5**) and isocaffeine (**6**)] (Table VIII) enables us to assess the effects on the geometry of the purine nucleus of different modes of substitution, particularly the

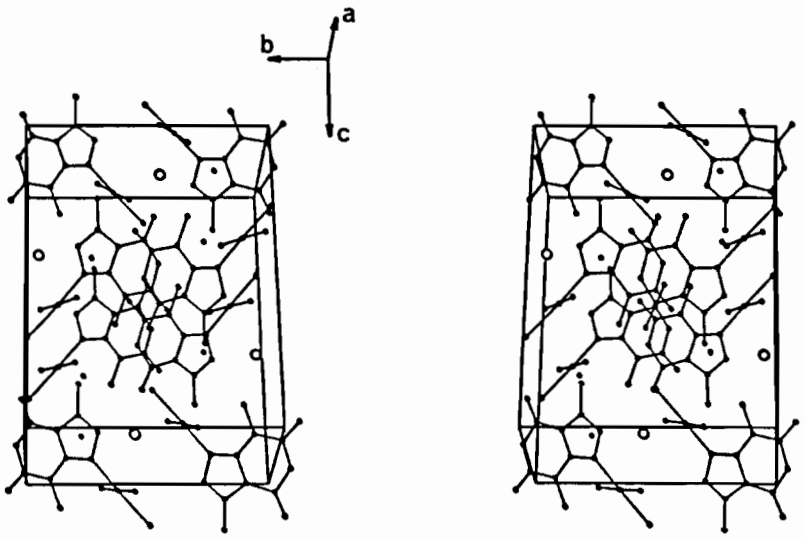


Fig. 3. Stereoscopic view of the packing of the molecules and ions for K[Pt(theobromine)Cl_3]·H_2O.

coordination of a Pt atom. Surprisingly, we see, at the level of the statistical significance of the data we have compared, no differences in the bond distances within the purine nucleus for any of these compounds. This structural equivalence, though not shown in Table VIII, also extends to the bond distances to the ring substituents where the substituent atoms are equivalent. Analysis for other, related structures not tabulated here [7, 9] shows they also conform to this pattern.

The values for the inter-bond angles again show a remarkable degree of internal consistency for these structures (Table VIII). However, there are some noticeable perturbations. In **1** the internal ring angle at N(1) (129.7(6)°) is larger than in the other structures. This could be attributable to the absence of a methyl substituent at this position. A similar effect can also be seen at N(7) in isocaffeine (**6**) where the angle is reduced. In **1** and **4**, where platinum is bonded to N(9), the angles at C(4) and N(9) are enlarged. It should be noted, however, that in all cases these effects are small and are at the margins of statistical significance.

In summary, the effects of varying substitution, in particular platinum, on the geometry of the purine nucleus appear, in our view, to be largely steric, rather than electronic, in origin.

Molecular Packing in the Crystals

Figure 3 shows the packing of the molecules and ions for **1**. The most significant feature of the packing is the formation of dimeric overlapping pairs of base units. Projected onto the mean plane of the purine ring there is virtually perfect overlap between symmetry-related pyrimidine rings with minimum interpair atomic separation of 3.27 Å. The $PtCl_3$ units can also be seen to form pairs related in a similar way, though in this instance the interplanar separation is 4.1 Å.

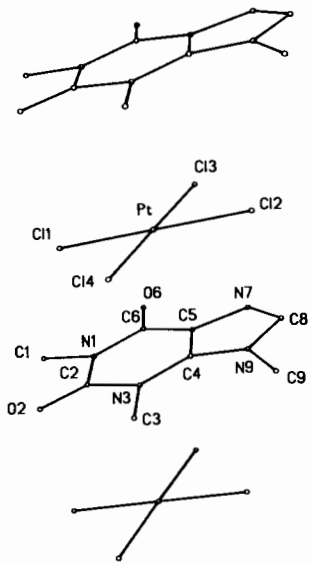


Fig. 4. Part of the infinite stack of $PtCl_4^{2-}$ anions and protonated isocaffeine cations in the structure of K(isocaffeinium)[$PtCl_4$]·H_2O, with the crystallographic numbering scheme.

In **2** there is no stacking of either the PtL_4 units or purine rings.

In **3** the $PtCl_4^{2-}$ anions and the protonated isocaffeine cations form an infinite alternating, overlapping stack along the crystallographic *a* direction (Fig. 4). Figure 5 shows the view of the rings immediately above and below one of the $PtCl_4^{2-}$ anions viewed normal to the $PtCl_4$ plane. The minimum

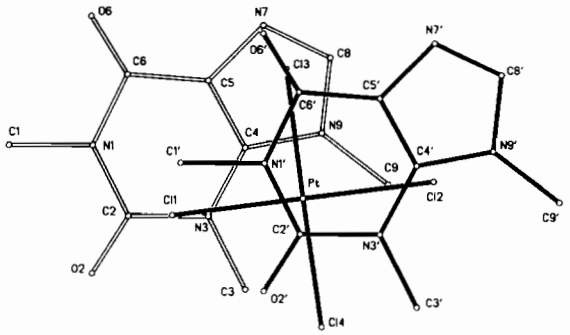


Fig. 5. Figure 4 viewed normal to the $PtCl_4^{2-}$ plane.

TABLE X. Coordination Distances of K^+

Structure	Atom	Distance (Å) (e.s.d. < 0.01 Å)
1	Cl(1)	3.19
	Cl(1′)	3.18
	Cl(2)	3.24
	Cl(3)	3.17
	O(6)	2.62
	OH	2.69
3	Cl(1)	3.23
	Cl(4)	3.25
	Cl(2′)	3.19
	Cl(3′)	3.15
	O(2′)	2.70
	O(6′)	2.71
	O(10′)	2.83

interlayer atomic separations are 3.37 Å between Cl(2) and C(4′), and 3.44 Å between Cl(1) and N(3).

Table X gives the coordination distances to the K^+ ions in **1** and **3**, and Table XI summarizes the hydrogen bonding geometries in all three structures.

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TABLE XI. Hydrogen Bonding Geometries

Structure	Atoms		R(X···Y) (Å)	R(H···Y) (Å)	X-H···Y (°)
	X	Y			
1	OH	O(2)	2.91	[a]	[a]
	OH	K	2.69	[a]	[a]
2	O(1A)	Cl	3.27	2.32	163
	O(1A)	O(2)	2.92	1.98	161
	O(1B)	O(2)	2.98	2.02	165
	O(1B)	O(6)	3.01	2.12	150
3	N(7)	O(6)	2.89	2.18	128
	O(10)	Cl(4)	3.21	2.47	132
	O(10)	Cl(3)	3.20	2.31	151

[a]Hydrogen atom positions not located.

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