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Simultaneous binding of soft and hard metals to a pyrimidine nucleobase: *trans*-$K_2[PtI_2(1\text{-}MeU)_2]\cdot 6H_2O$, an anionic Pt-1-methyluracil (1-MeU) complex arranged in circles

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Abstract

The anionic complex *trans*-$[PtI_2(1\text{-}MeU\text{-}N3)_2]^{2-}$ (1-MeU = 1-methyluracil anion, $C_5H_5N_2O_2$), as its K salt, forms a supramolecular assembly with anionic entities linked via K^+ cations and bridging H_2O molecules. The Pt coordination sphere is normal square-planar. Crystallographic data are as follows: $C_{10}H_{22}I_2K_2N_4O_{10}Pt$, rhombohedral, space group $R\bar{3}$, $a = 26.166(4)$, $c = 9.245(2)$ Å, $U = 5482(3)$ Å^3, $Z = 9$. The structure was refined to $R = 3.46$, $R_w = 4.63$ for 1813 unique reflections with $I > 3\sigma(I)$.

Key words: Crystal structures; Platinum complexes; Uracil complexes; Nucleobase complexes; Anionic complexes

Introduction

Thymine and uracil nucleobases, when metalated at the deprotonated N3 position, bind additional metal ions through the exocyclic oxygens [1]. This principle is also realized in a number of multinuclear complexes derived from cyclic amides [2]. As far as N3 bound Pt^{II} is concerned, the various examples of homo- and heteronuclear derivatives reported from our laboratory were derived either from neutral a_2PtL_2 complexes (a = NH_3 or amine, a_2 = diamine, L = 1-methyluracil or 1-methylthymine anion, geometry *cis* [1d] or *trans* [3]) or cationic species of types *cis*-$[a_2PtL_2Pta_2]^{2+}$ (two L ligands arranged head–tail [4] or head–head [5]) and *cis*-$[a_2PtLL']^+$ (L′ = neutral 1-methylcytosine nucleobase [6]).

In this report we describe the preparation and crystal structure of *trans*-$K_2[PtI_2(1\text{-}MeU)_2]\cdot 6H_2O$, which can be considered a heteronuclear derivative of the anionic *trans*-$[PtI_2(1\text{-}MeU)_2]^{2-}$ entity. The compound has considerable potential as a building block for multinuclear Pt complexes of uracil, and work is underway to explore the chemistry of this compound in greater depth.

Experimental

The compound was prepared from K_2PtCl_4 (3 mmol dissolved in 50 ml of water) upon addition of KI (12 mmol dissolved in 17 ml of water) and slow addition of an aqueous solution of $K^+(1\text{-}MeU)^-$ (7 mmol in 20 ml of water, prepared *in situ* upon addition of 1 equiv. of KOH to 1-MeUH). Precipitated PtI_2 was filtered off after 1 day at 30 °C, and the reaction mixture (pH 9) then allowed to evaporate very slowly at 30 °C. Large orange–red single crystals formed in 42% yield within several weeks. *Anal.* Calc. for $K_2[PtI_2(C_5H_5N_2O_2)_2]\cdot 6H_2O$: C, 13.6; H, 2.5; N, 6.3. Found: C, 13.6; H, 2.2; N, 6.3%. Scanning electron microscopy analysis was consistent with the presence of Pt, K and I. IR: ν (cm^{-1}) (KBr): 1637vs, 1568vs, 1542sh, 1450vs, 1364vs, 1330vs. ^{1}H NMR (Bruker AC200; 200 MHz): δ (ppm) (D_2O, pD = 6.4): 7.30 (H6), 5.57 (H5), 3.33 (N–CH_3); ^3J(H5–H6) 7.23 Hz. Doubling of H6 and H5 ($\Delta\delta = 2.3$ Hz) is observed and attributed to the existence of two rotamers in solution.

$C_{10}H_{22}I_2K_2N_4O_{10}Pt$, $M = 885.4$, rhombohedral, space group $R\bar{3}$, $a = 26.166(4)$, $c = 9.245(2)$ Å, $U = 5482(3)$ Å^3, $Z = 9$, $D_c = 2.414$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 8.68$ mm^{-1}, crystal size 0.40×0.35×0.15 mm, $T = 294$ K,

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

	x	y	z	U_{eq}[a]
Pt(1)	0	5000	5000	39(1)
I(1)	82(1)	4106(1)	5966(1)	57(1)
K(1)	1503(1)	5368(2)	6077(3)	102(2)
N(3)	−142(3)	5199(3)	7054(6)	42(3)
C(4)	−699(4)	4962(4)	7541(8)	47(4)
O(4)	−1135(3)	4604(3)	6789(6)	62(3)
C(5)	−790(5)	5133(4)	8964(9)	59(5)
C(6)	−334(5)	5504(4)	9705(9)	63(5)
N(1)	223(3)	5738(3)	9212(7)	53(3)
C(1)	716(5)	6165(4)	10067(10)	73(5)
C(2)	331(4)	5576(4)	7850(8)	50(4)
O(2)	840(3)	5782(3)	7421(7)	69(3)
O(5)	1728(4)	4829(4)	8393(10)	103(5)
O(6)	1176(4)	635(4)	5014(17)	157(7)
O(7)[b]	2426(14)	5336(11)	4832(28)	118(19)
O(71)[b]	2724(15)	5715(12)	5000(43)	159(22)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Population parameter 0.5.

TABLE 2 Bond lengths (Å) and angles (°)

Pt(1)–I(1)	2.610(1)	Pt(1)–K(1)	3.688(3)
Pt(1)–N(3)	2.052(6)	Pt(1)–I(1a)	2.610(1)
Pt(1)–K(1a)	3.688(3)	Pt(1)–N(3a)	2.052(6)
K(1)–O(2)	2.760(10)	K(1)–O(5)	2.783(12)
K(1)–O(7)	2.714(37)	K(1)–O(71)	3.019(39)
K(1)–O(4a)	2.834(7)	K(1)–O(5a)	2.992(13)
K(1)–O(7a)	2.997(28)	K(1)–O(71a)	3.187(33)
N(3)–C(4)	1.345(11)	N(3)–C(2)	1.351(9)
C(4)–O(4)	1.261(9)	C(4)–C(5)	1.447(13)
O(4)–K(1a)	2.834(7)	C(5)–C(6)	1.295(12)
C(6)–N(1)	1.347(14)	N(1)–C(1)	1.447(11)
N(1)–C(2)	1.403(11)	C(2)–O(2)	1.224(12)
O(5)–K(1c)	2.992(12)	O(7)–O(71)	0.917(34)
O(7)–K(1c)	2.997(33)	O(71)–K(1c)	3.187(40)
I(1)–Pt(1)–N(3)	91.0(2)	I(1)–Pt(1)–I(1a)	180.0(1)
I(1)–Pt(1)–N(3a)	89.0(2)	Pt(1)–N(3)–C(4)	119.0(5)
Pt(1)–N(3)–C(2)	118.2(6)	C(4)–N(3)–C(2)	122.8(7)
N(3)–C(4)–O(4)	121.8(8)	N(3)–C(4)–C(5)	117.9(7)
O(4)–C(4)–C(5)	120.3(8)	C(4)–C(5)–C(6)	118.7(10)
C(5)–C(6)–N(1)	123.0(9)	C(6)–N(1)–C(1)	120.7(8)
C(6)–N(1)–C(2)	120.2(7)	C(1)–N(1)–C(2)	119.2(8)
N(3)–C(2)–N(1)	117.3(8)	N(3)–C(2)–O(2)	122.9(8)
N(1)–C(2)–O(2)	119.7(7)	N(3)–Pt(1)–N(3a)	180.0(1)
O(2)–K(1)–O(5)	100.8(3)	O(5)–K(1)–O(7)	83.9(7)
O(5)–K(1)–O(71)	87.0(8)	O(2)–K(1)–O(4a)	97.0(3)
O(7)–K(1)–O(4a)	85.6(6)	O(71)–K(1)–O(5a)	95.9(7)
O(5)–K(1)–O(7a)	72.0(7)	O(7)–K(1)–O(7a)	106.6(10)
O(71)–K(1)–O(7a)	91.4(9)		

[a] For symmetry codes see legend of Fig. 2.

$F(000) = 3708$, $3 \leqslant 2\theta \leqslant 53°$, $R(R_w) = 3.46$ (4.73) for 1813 unique reflections with $I > 3\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares analysis. Atoms were refined anisotropically, protons were situated at calculated positions in the uracil moiety and refined by the method used in SHELXTL as rigid groups with the atoms they are connected to. The protons of the bridging water molecules were not determined. Occupancies of O(7) and O(71) were left to refine independently and converged practically at 0.5. The corresponding non-centrosymmetric space group $R3$ was tested, but the refinement was unstable and very high correlation matrix elements appeared. The intensity statistics also strongly supported $R\bar{3}$. Atomic coordinates, and bond lengths and angles are given in Tables 1 and 2, respectively. See also 'Supplementary material'.

Results

Figure 1 provides a view of *trans*-$K_2[PtI_2(1\text{-MeU-}N3)_2]$ with water molecules omitted. The compound is centrosymmetric. Pt binding is via the deprotonated N(3) positions of two 1-MeU anions. Pt–N (2.052(6) Å) and Pt–I (2.610(1) Å) distances are not unusual, the latter reflecting the *trans* influence of iodide [7]. The two K^+ cations are coordinated pairwise by exocyclic O(2) and O(4) oxygens of the two uracils, which are coplanar. The two K^+ are at different sides relative to the $Pt(1\text{-MeU})_2$ plane, with a deviation of 1.484 Å from the plane formed by O(2), O(4), O(2a) and O(4a). As a consequence of this arrangement Pt–K distances become fairly long, 3.688(3) Å. The arrangement of the three metal ions relative to the 1-MeU rings makes this compound distinctly different from structurally related compounds like *trans*-$[(NH_3)_2Pt(1\text{-MeU})_2Ag_2]^{2+}$ [3] and *trans*-$[a_2Pt(1\text{-MeC}^-)_2M_x]^{n+}$ ($a = NH_3$ or CH_3NH_2; 1-MeC$^-$ = 1-methylcytosine deprotonated at N(4); M = Pd, $x = 1$ [8]; M = Hg, $x = 1$ [9]; M = Ag, $x = 2$ [10]), where the heterometal is essentially coplanar with

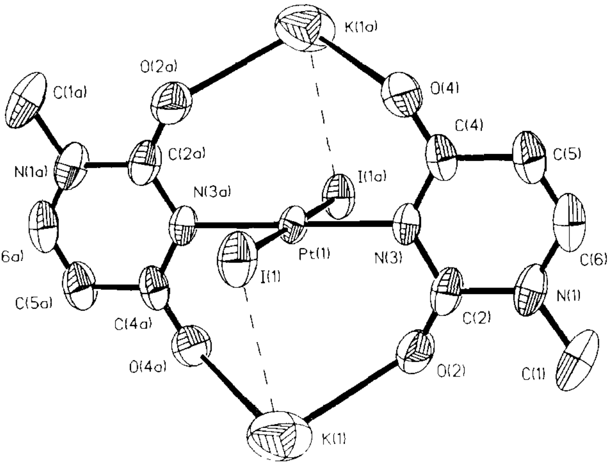

Fig 1. Title compound with atom numbering scheme. H_2O molecules are not shown.

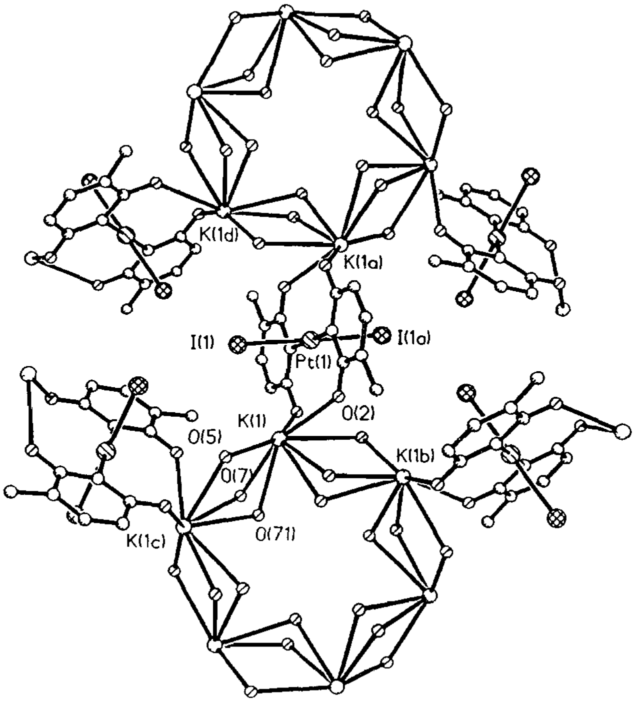

Fig. 2 Cyclic arrangement of *trans*-$K_2[PtI_2(1\text{-}MeU)_2]\cdot 4H_2O$. Water molecules O(7) and O(71) have occupancies of 0.5 each. Two additional H_2O molecules per molecule (O(6)) are omitted for clarity. Symmetry codes are as follows: a $= -x, -y+1, -z+1$; b $= y-\frac{1}{3}, -x+y+\frac{1}{3}, -z+\frac{4}{3}$, c $= x-y+\frac{2}{3}, x+\frac{1}{3}, -z+\frac{4}{3}$; d $= -y+\frac{1}{3}, x-y+\frac{2}{3}, z-\frac{1}{3}$

PtL_2 (L = 1-MeU or 1-MeC^-), thereby permitting short Pt–M contacts and metal–metal bond formation.

The coordination sphere of K, apart from bonds to O(2) (2.760(10) Å) and O(4) (2.834(7) Å), is completed by bonds to water molecules, which serve as bridges to adjacent potassiums (Fig. 2). Of the six bridging water oxygens per K, O(5) is fully occupied while O(7) and O(71) have populations 0.5 each. The water molecules O(6) are located between the star-like O–K–O rings. They are H bonded to each other (2.667 Å) and to exocyclic O(4) oxygens (2.748 Å) (Fig. 3).

The positions of the iodide ligands of Pt relative to K^+ and a comparison of the K–I separations (3.520(3) Å) with effective ionic radii of K^+ (1.65 Å) and I^- (2.06 Å) [11] suggest additional weak interactions. As seen in Fig. 2 and evident from the stereoview given in Fig. 3, the arrangement of K^+ and bridging water molecules generate a star-like supramolecular assembly with $[PtI_2(1\text{-}MeU)_2]^{2-}$ anions threaded by K^+ cations and bridging water molecules in circles. These circles are separated by hexagons of H_2O (6) molecules. Both entities generate pores along the *c* axis.

The *trans* geometry of the title compound is noteworthy in that it is unexpected on the basis of the kinetic *trans* effect, which should have produced the *cis* product, very much as in the case of the preparation of *cis*-a_2PtI_2 (a = NH_3 [7a] or creatinine [7b]) from K_2PtI_4 and a. On the other hand, there is ample evidence [12] that steric restraints can overrule the *trans* effect.

Preliminary work on the chemistry of the title compound confirms expectations on the easy replacement of K^+ by other heterometals, is indicative of redox reactions with $PtCl_6^{2-}$, and suggests formation of multinuclear Pt–(1-MeU) complexes after abstraction of the iodo ligands. Work on these topics is in progress in our laboratory.

Supplementary material

Experimental crystallographic details, anisotropic displacement coefficients of heavy atoms, H atoms co-

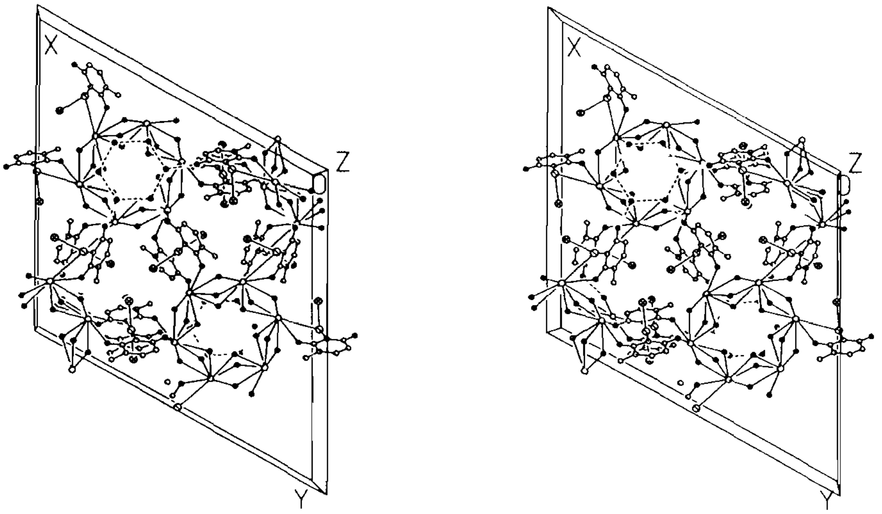

Fig. 3. Stereoview of the title compound with water molecules O(6) included Six O(6) water molecules form hexagons with H bonds between each other and with O(4) oxygens of 1-MeU ligands

ordinates, isotropic displacement coefficients, observed and calculated structure factors can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, under CSD 400329 on request. Requests should be accompanied by the complete literature citation.

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References

1 (a) F. Guay and A.L. Beauchamp, *J Am. Chem. Soc., 101* (1979) 6260; (b) B. Lippert and D. Neugebauer, *Inorg. Chim Acta, 46* (1980) 171; (c) F Guay and A.L. Beauchamp, *Inorg Chim. Acta, 66* (1982) 57, (d) K. Aoki and W. Saenger, *Acta Crystallogr., Sect. C, 40* (1984) 775; (e) B. Lippert, *Prog. Inorg. Chem, 37* (1989) 1.

2 (a) D.M.L. Goodgame, S.P.W. Hill and D.J. Williams, *Polyhedron, 11* (1992) 1841, and refs. therein; (b) A.J. Blake, R.O. Gould, P.E.Y. Milne and R.E.P. Winpenny, *J Chem Soc, Chem. Commun,* (1992) 522.

3 H. Schöllhorn, U. Thewalt and B. Lippert, *J. Chem Soc, Chem Commun.,* (1984) 769.

4 U. Thewalt, D. Neugebauer and B. Lippert, *Inorg Chem., 23* (1984) 1713.

5 (a) B. Lippert, H. Schollhorn and U. Thewalt, *Inorg Chem, 26* (1987) 1736; (b) B Lippert and D. Neugebauer, *Inorg. Chem., 21* (1982) 451.

6 (a) B. Lippert, U. Thewalt, H. Schollhorn, D.M.L. Goodgame and R.W. Rollins, *Inorg. Chem., 23* (1984) 2807; (b) H. Schöllhorn, U. Thewalt and B. Lippert, *Inorg. Chim Acta, 135* (1987) 155.

7 (a) G. Raudaschl-Sieber, B. Lippert, J.F. Britten and A.L Beauchamp, *Inorg Chim Acta, 124* (1986) 213; (b) P.T. Beurkens, A. Perales, F.J. Martin-Gil and J. Martin-Gil, *Monatsh Chem., 119* (1988) 1189.

8 (a) M. Krumm, B. Lippert, L. Randaccio and E. Zangrando, *J Am. Chem Soc., 113* (1991) 5129; (b) M. Krumm, E. Zangrando, L. Randaccio, S. Menzer and B. Lippert, *Inorg Chem., 32* (1993) 700.

9 M. Krumm, E. Zangrando, L. Randaccio, S. Menzer, A. Danzmann, D. Holthenrich and B Lippert, *Inorg Chem, 32* (1993) 2183.

10 D. Holthenrich, M. Krumm, E. Zangrando, L. Randaccio and B Lippert, unpublished results.

11 R.D. Shannon and C.T. Prewitt, *Acta Crystallogr, Sect. B, 25* (1969) 925.

12 (a) C.J.L. Lock and M Zvagulis, *Acta Crystallogr, Sect. B, 36* (1980) 2140; (b) A.M. Beja, J.A.C. Paixao, J.M. Gil and M.A. Salgado, *Acta Crystallogr, Sect. C, 47* (1991) 2333.