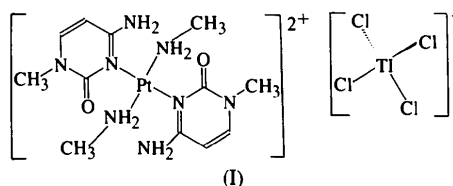


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Randaccio, Menzer, Danzmann, Holthenrich & Lippert, 1993). The rings of the 1-MeC<sup>-</sup> ligands bridging the metals present the same orientation with respect to the N—Pt—N vector (a head-to-head arrangement). Attempts at obtaining similar heterobimetallic complexes containing Tl<sup>III</sup> were unsuccessful and led to the formation of the title compound.



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### *trans*-Bis(methylamine-*N*)bis(1-methylcytosine-*N*<sup>3</sup>)platinum(II) Bis[tetrachlorothallate(III)]

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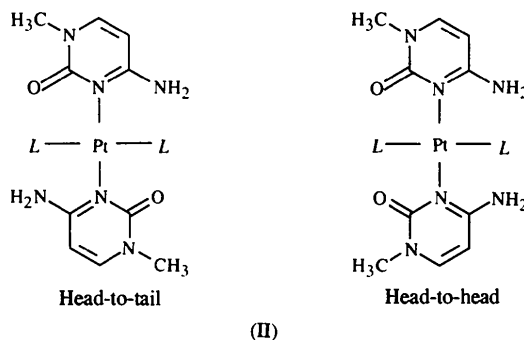
#### Abstract

The crystal structure of the title compound, *trans*-bis(methylamine-*N*)bis(4-amino-1-methyl-2(1*H*)-pyrimidinone-*N*<sup>3</sup>)platinum(II) bis[tetrachlorothallate(III)], [Pt(CH<sub>3</sub>N)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>2</sub>][TlCl<sub>4</sub>]<sub>2</sub>, consists of square-planar Pt<sup>II</sup> cations arranged on a crystallographic inversion center and distorted tetrahedral TlCl<sub>4</sub><sup>-</sup> anions. The compound is very similar to known cytosine complexes of the *trans*-[(NH<sub>3</sub>)<sub>2</sub>Pt(1-methylcytosine)<sub>2</sub>]*X*<sub>2</sub> type. The distortion in TlCl<sub>4</sub><sup>-</sup> and in other anion-containing compounds is discussed.

#### Comment

The title compound, (I), was obtained during our continuing research on the chemistry of heterobimetallic complexes bridged by cytosinate ligands (amino deprotonated, hereinafter 1-MeC<sup>-</sup>). These complexes have the general formulae *trans*-[(NH<sub>3</sub>)<sub>2</sub>Pt(1-MeC<sup>-</sup>)<sub>2</sub>PdL](NO<sub>3</sub>)<sub>*n*</sub> (*L* is a neutral or anionic ligand; Krumm, Lippert, Randaccio & Zangrando, 1991; Krumm, Zangrando, Randaccio, Menzer & Lippert, 1993; Mealli, Pichierri, Randaccio, Zangrando, Krumm, Holthenrich & Lippert, 1995) and *trans*-[(NH<sub>3</sub>)<sub>2</sub>Pt(1-MeC<sup>-</sup>)<sub>2</sub>Hg]*X*<sub>2</sub> (*X* is Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>; Krumm, Zangrando,

In the complex cation of (I), the Pt atom is positioned on a crystallographic inversion center resulting in a head-to-tail arrangement of cytosine rings (Fig. 1). The Pt—N3 (of 1-MeC) and Pt—N5 (of amine) bond lengths are 2.023 (6) and 2.046 (7) Å, respectively. The coordination around N3 is distorted, with the Pt—N3—C4 angle [121.8 (5)°] significantly larger than the Pt—N3—C2 angle [117.6 (5)°]. The two coplanar 1-MeC ligands are mutually *trans* with respect to rotation about the N3—Pt—N3' vector and form large dihedral angles of 73.9 (2)° with the N<sub>4</sub> coordination plane, possibly for steric reasons. The cation geometry is very similar to that reported for the corresponding bis(amino) complex *trans*-[(NH<sub>3</sub>)<sub>2</sub>Pt(1-MeC)<sub>2</sub>]<sup>2+</sup> (NO<sub>3</sub><sup>-</sup> salt: Lippert, Lock & Speranzini, 1981; ClO<sub>4</sub><sup>-</sup> salt: Brown & Lock, 1988) where the same orientation of the nucleobases has been observed. Although the present Pt complex, when isolated from aqueous solution by slow evaporation, displays the cytosine bases in a head-to-tail arrangement, the corresponding head-to-head rotamer, with the cytosines in the same orientation, has also been isolated (Holthenrich, Sóvágó, Fusch, Erxleben, Fusch, Rombeck & Lippert, 1995).



The geometry of the TlCl<sub>4</sub><sup>-</sup> anion is characterized by two longer [Tl—Cl1 2.440 (2) and Tl—Cl2 2.421 (3) Å] and two shorter [Tl—Cl3 2.395 (2) and Tl—Cl4 2.402 (2) Å] distances. Correspondingly, the Cl1—Tl—Cl2 and Cl3—Tl—Cl4 angles are 111.2 (1) and 121.9 (1)°, respectively, with the other angles

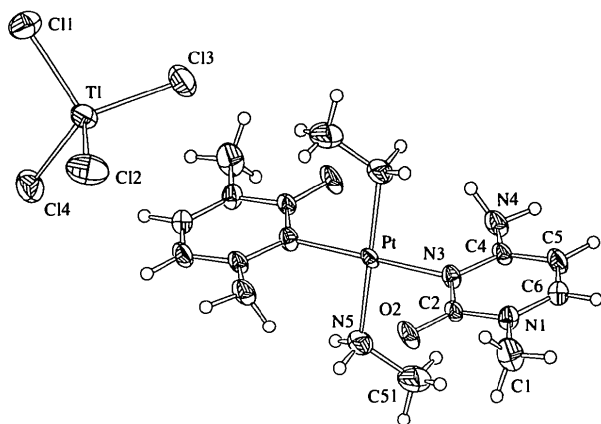


Fig. 1. ORTEP drawing (Johnson, 1976) of (I) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

at Tl ranging from 103.7(1) to 109.1(1)°. This squashed tetrahedral structure is similar to that found in  $C_6H_5N^+ \cdot TlCl_4^-$  (Millikan, Mackay, James & Bastow, 1988), where the  $C_{2v}$  symmetry cation exhibits two longer Tl—Cl bonds of 2.423 (7) Å, subtending an angle of 124.7 (4)°, and two shorter distances of 2.395 (7) Å, subtending an angle of 113.0 (4)°. Few other examples of  $TlCl_4^-$  anions have been reported, their geometries varying from exact  $T_d$  symmetry (Kahwa, Miller, Mitchel, Fronczek, Goodrich, Williams, O'Mahoney, Slawin, Ley & Groombridge, 1992), with Tl—Cl bond lengths of 2.393 (3) and 2.42 (1) Å, to  $C_{3v}$  symmetry (Lenck, Dou & Weiss, 1991), with one Tl—Cl distance of 2.388 Å, three Tl—Cl2 distances of 2.400 Å and Cl1—Tl—Cl2 and Cl2—Tl—Cl2' angles of 107.7 and 111.2°, respectively. Lower  $C_{2v}$  and  $C_s$  symmetries, although less distorted, have been found in two compounds, namely  $KTiCl_4$  (Glaser, 1980) and  $trans-[(ethylenediamine)_2Co^{III}Cl_2][TiCl_4]$  (Brodersen, Rath & Thiele, 1972). In the latter, the distances vary from 2.412 (2) to 2.423 (2) Å and the angles from 106.6 to 113.2°, whereas in the former, all the Tl—Cl distances are equal at 2.433 (3) Å, but two angles of 114.8 (1) and 106.9 (1)° are observed. Such a variability in the  $TlCl_4^-$  geometry is even more pronounced than that observed in  $CuCl_4^{2-}$  (Kahwa *et al.*, 1992), whose geometry varies from the apparent average room-temperature  $T_d$  symmetry to variously distorted  $D_{2d}$  geometries, the shorter Cu—Cl distances being observed in the ion of highest symmetry, as in the  $TlCl_4^-$  anion.

## Experimental

$trans-[(CH_3NH_2)_2Pt(1-MeC_2)](NO_3)_2$  (0.101 g, 0.16 mmol) was dissolved in water (10 ml) and  $TlCl_3$  (0.0497 g, 0.16 mmol) was added. The title compound crystallized within 3 d at 295 K in 31% yield. Crystals suitable for analysis were obtained by recrystallization from aqueous solution. Accord-

ing to IR spectroscopy, the colorless precipitate is identical to the crystal isolated. Analysis found: C 12.4, H 2.1, N 10.0, Cl 23.9%; calculated: C 12.0, H 2.0, N 9.3, Cl 23.6%.

## Crystal data

$[Pt(CH_3N)_2(C_5H_7N_3O)_2] \cdot [TiCl_4]_2$   
 $M_r = 1199.83$   
 Monoclinic  
 $P2_1/n$   
 $a = 7.4346$  (10) Å  
 $b = 15.8698$  (10) Å  
 $c = 12.5590$  (10) Å  
 $\beta = 96.91$  (1)°  
 $V = 1471.0$  (3) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 2.709$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Mo K $\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 25 reflections  
 $\theta = 11.9$ – $20.9$ °  
 $\mu = 16.43$  mm<sup>-1</sup>  
 $T = 293$  K  
 Cubic  
 $0.30 \times 0.25 \times 0.20$  mm  
 Colorless

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  $\psi$  scan (North, Phillips & Mathews, 1968)  
 $T_{min} = 0.028$ ,  $T_{max} = 0.037$   
 4284 measured reflections  
 4246 independent reflections

2638 observed reflections [ $I > 3\sigma(I)$ ]  
 $R_{int} = 0.030$   
 $\theta_{max} = 30$ °  
 $h = -10 \rightarrow 10$   
 $k = 0 \rightarrow 22$   
 $l = 0 \rightarrow 17$   
 3 standard reflections  
 frequency: 66.6 min  
 intensity decay: none

## Refinement

Refinement on  $F$   
 $R = 0.0351$   
 $wR = 0.0384$   
 $S = 1.08$   
 2638 reflections  
 151 parameters  
 H-atom parameters not refined  
 $w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.01$   
 $\Delta\rho_{max} = 1.13$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -1.93$  e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A, 2.2C and 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Pt	1/2	1/2	1/2	0.0194 (1)
O2	0.2100 (7)	0.6318 (4)	0.5232 (5)	0.036 (2)
N1	0.3688 (9)	0.7515 (4)	0.5673 (5)	0.025 (2)
N3	0.5154 (8)	0.6258 (4)	0.5253 (5)	0.023 (2)
N4	0.8214 (9)	0.6231 (5)	0.5148 (6)	0.033 (2)
C1	0.2003 (12)	0.7951 (6)	0.5821 (9)	0.043 (3)
C2	0.3577 (9)	0.6677 (5)	0.5376 (6)	0.023 (2)
C4	0.6758 (9)	0.6674 (5)	0.5347 (6)	0.024 (2)
C5	0.6859 (10)	0.7527 (5)	0.5661 (7)	0.029 (3)
C6	0.5314 (11)	0.7912 (5)	0.5801 (7)	0.029 (3)
N5	0.3872 (11)	0.5143 (5)	0.3442 (6)	0.041 (2)
C51	0.4279 (17)	0.5913 (8)	0.2839 (8)	0.059 (4)
Tl	0.34667 (5)	0.07767 (2)	0.65821 (3)	0.0360 (1)
Cl1	0.4253 (4)	-0.0383 (2)	0.7828 (2)	0.0526 (8)
Cl2	0.0746 (4)	0.1488 (2)	0.6981 (2)	0.0614 (9)
Cl3	0.5984 (4)	0.1722 (2)	0.6909 (2)	0.0537 (8)
Cl4	0.2598 (4)	0.0161 (2)	0.4849 (2)	0.0511 (8)

Table 2. Selected geometric parameters (Å, °)

Pt—N3	2.023 (6)	Ti—Cl2	2.421 (3)
Pt—N5	2.046 (7)	Ti—Cl3	2.395 (2)
Ti—Cl1	2.440 (2)	Ti—Cl4	2.402 (2)
N3—Pt—N5	92.9 (3)	Cl2—Ti—Cl4	103.7 (1)
Pt—N3—C4	121.8 (5)	Cl2—Ti—Cl3	109.1 (1)
Pt—N3—C2	117.6 (5)	C11—Ti—Cl4	107.0 (1)
Pt—N5—C51	119.5 (6)	C11—Ti—Cl3	103.9 (1)
Cl3—Ti—Cl4	121.9 (1)	C11—Ti—Cl2	111.2 (1)

The highest difference Fourier peak and deepest trough were located near the Pt and Ti atoms, respectively.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CELDIM* (Enraf-Nonius, 1989). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## *trans*-Bis(benzoato-*O,O'*)bis(*N,N*-diethylnicotinamide-*N*<sup>1</sup>)copper(II)

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## Abstract

The title molecule, [Cu(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O)<sub>2</sub>], is a crystallographically centrosymmetric mononuclear complex. The two benzoate ions are coordinated to the Cu atom as bidentate ligands. The N and nearest O atoms form a square-planar arrangement around the Cu atom, with the tetragonally distorted octahedral coordination completed by the remaining two carboxylate O atoms.

## Comment

*N,N*-Diethylnicotinamide (DENA) is an important respiratory stimulant (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1972). The structures of some complexes obtained from the reactions of transition metal(II) ions with DENA have been determined previously; [Cu<sub>2</sub>(DENA)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>COO)<sub>4</sub>] (Hökelek, Necefoğlu & Balcı, 1995), [Zn<sub>2</sub>(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>4</sub>(DENA)<sub>2</sub>].2H<sub>2</sub>O (Hökelek & Necefoğlu, 1996), [Mn(DENA)<sub>2</sub>(NCS)<sub>2</sub>] (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1973*a*), [Zn(DENA)<sub>2</sub>(NCS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1973*b*) and [Cd(DENA)(SCN)<sub>2</sub>] (Bigoli *et al.*, 1972). In [Mn(DENA)<sub>2</sub>(NCS)<sub>2</sub>], DENA is a bidentate ligand, while in [Cu<sub>2</sub>(DENA)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>COO)<sub>4</sub>], [Zn<sub>2</sub>(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>4</sub>(DENA)<sub>2</sub>].2H<sub>2</sub>O, [Cd(DENA)(SCN)<sub>2</sub>] and [Zn(DENA)<sub>2</sub>(NCS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], DENA is a monodentate ligand. In [Cu<sub>2</sub>(DENA)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>COO)<sub>4</sub>], the benzoate ion acts as a bidentate ligand, but in [Zn<sub>2</sub>(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>4</sub>(DENA)<sub>2</sub>].2H<sub>2</sub>O, two of the benzoate ions act as monodentate ligands, while the other two are bidentate, bridging the two Zn atoms. A series of Cu<sup>II</sup> alkyl and aryl carboxylates in which the carboxylate is monodentate, cyclic bidentate or bridging, depending on the amount and coordination ability of the solvent molecule, has been reported in the literature (Meln'k, 1981, 1982; Davey & Stephens, 1971*a,b*; Musaev, Movsumov, Mamedov & Amirasanov, 1979; Usabaliev *et al.*, 1980, 1981; Hökelek *et al.*, 1995; Hökelek & Necefoğlu, 1996). The factors influencing the formation of either binuclear or mononuclear carboxylate complexes of Cu<sup>II</sup> have been investigated, but still no clear understanding exists (Meln'k, 1981). As determined previously, Cu<sup>II</sup> benzoate forms two types of adduct with DENA, as it