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Simultaneous binding of soft and hard metals to a pyrimidine nucleobase: preparation and X-ray structure of $[(en)Pd(1\text{-}MeT)_2Na_2](NO_3)_2\cdot H_2O$ (1-MeT = 1-methylthymine anion)

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Abstract

The crystal structure of $[(en)Pd(1\text{-}MeT)_2Na_2](NO_3)_2\cdot H_2O$, where 1-MeT = 1-methylthymine anion, $C_6H_7N_2O_2$, is reported. The compound crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 8.203(1)$, $b = 20.908(5)$, $c = 13.644(5)$ Å, $\beta = 98.35(2)°$, $V = 2316(2)$ Å^3. Pd binding is through N3 of the two 1-MeT rings. The two Na^+ are coordinated to two O4 and two O2 oxygens of the 1-MeT rings, respectively. The compound represents the first structurally characterized example of M,M'_2 stoichiometry derived from a *cis*-a_2ML_2 compound.

Keywords: Crystal structures; Palladium complexes; Nucleobase complexes

1. Introduction

Our interest in the metal coordination properties of nucleobases in general [1] and of pyrimidine nucleobases in particular [2] has led us, among others, also to mixed metal (Pt,M_x) complexes of varying stoichiometries. For example, from *cis*-$(NH_3)_2PtL_2$ (L = 1-methyluracil anion, 1-MeU, or 1-methylthymine anion, 1-MeT) mixed metal complexes of the following stoichiometries have been prepared and X-ray structurally characterized: Pt,M,L_2, Pt_2,M,L_4 and Pt_4,M,L_4. Different stoichiometries have been obtained from derivatives of dinuclear (head–tail) *cis*-$[(NH_3)_2PtL_2Pt(NH_3)_2]^{2+}$, e.g. Pt_2,M_2,L_2 [3], or from *trans*-$(NH_3)_2PtL_2$, e.g. Pt,M_2,L_2 [4]. Finally, from the mixed nucleobase complex *cis*-$[(NH_3)_2PtLL']^+$ (L = 1-MeU, L′ = 1-methylcytosine, 1-MeC), compounds of $Pt_2(L,L')_2M$ [5] and of $Pt(L,L')M$ [6] stoichiometries were characterized. Very recently, we have discovered novel heteronuclear Pt,M,L''_2 complexes (L″ = N4 deprotonated 1-methylcytosine) having, however, a quite different structure [7]. Heteronuclear complexes derived from a *cis*-a_2PdL_2 compound (with L coordinated via N3) have not been reported as yet. In this paper, we describe the first example of a mixed Pd,Na_2,L_2 (L = 1-MeT) compound which, at the same time, is the first structurally characterized example of this stoichiometry in a *cis*-a_2ML_2 system. Previously prepared $NaNO_3$ adducts of related compounds, *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ [8] and $(tmeda)Pt(1\text{-}MeU)_2$ [9] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) were not structurally characterized. The only other relevant compounds are $CH_3Hg(1\text{-}MeT)\cdot 0.5NaNO_3$ [10] and *trans*-$K_2[PtI_2(1\text{-}MeT)_2]\cdot 6H_2O$ [11].

2. Experimental

2.1. Preparation

The preparation of $(en)Pd(1\text{-}MeT)_2\cdot 4H_2O$ (**1**) from $enPdCl_2$ and 1-MeTH has already been reported [12]. The isolated yield after Sephadex G-10 chromatography was 32% only because of the difficulty of removing $NaNO_3$ from **1**. Later fractions contained increasing amounts of $NaNO_3$ as evident from IR spectroscopy. A defined $NaNO_3$ adduct of **1** was obtained upon recrystallization of **1** from water in the presence of excess $NaNO_3$. Pale yellow columns of $[(en)Pd(1\text{-}MeT)_2Na_2](NO_3)_2\cdot H_2O$ (**2**) formed upon evaporation

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of the solution at 3 °C. *Anal.* Calc. for $C_{14}H_{24}N_8O_{11}Na_2Pd$: C, 26.57; H, 3.83; N, 17.71. Found: C, 26.0; H, 3.8; N, 17.5%. The major difference in IR spectra between **1** and **2** refers to nitrate (e.g. 1390 cm^{-1}) and H_2O bands ($\sim$3450 cm^{-1}) in accordance with the respective compositions.

2.2. X-ray crystallography

A suitable prismatic crystal of **2** was mounted on glass fiber at a random orientation. An Enraf-Nonius CAD4 diffractometer was used both for the unit cell and space group determination and for the data collection. Unit cell dimensions were obtained by least-squares fit of the 2θ values of 25 high order reflections ($9.2 < \theta < 15.6°$). Selected crystallographic and other relevant data are listed in Table 1.

Table 1
Experimental data for the X-ray diffraction study of $[(en)Pd(1\text{-}MeT)_2Na_2](NO_3)_2 \cdot H_2O$

Formula	$C_{14}H_{24}Na_2N_8O_{11}Pd$
Molecular weight	632.77
Crystal dimensions (mm)	0.17×0.25×0.55
Data collection, T (°C)	23
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.203(1)
b (Å)	20.908(5)
c (Å)	13.644(5)
β (°)	98.35(2)
V (Å^3)	2315(1)
Z	4
ρ_{calc} (g cm^{-3})	1.815
μ (cm^{-1})	8.957
Radiation, λ (Å)	Mo Kα (graphite monochromated), 0.71069
Measured reflections	$\pm h$, $+k$, $+l$
θ Range (°)	$2.5 < \theta < 27.0$
Scan type	$\omega/2\theta$
Scan width (°)	$1.20 + 0.35 \tan\theta$
Max. counting time (s)	70
Background time (s)	0.5×scan time
Max. scan speed (° min^{-1})	10.1
Prescan rejection limit	0.55 (1.80σ)
Prescan acceptance limit	0.030 (33.3σ)
Horizontal receiving slit (mm)	$1.70 + \tan\theta$
Vertical receiving slit (mm)	4.0
No. Independent data collected	5044
No. observed reflections (n_o) ($\|F_o\|^2 > 4.0\sigma(\|F\|^2)$)	4180
Transmission coefficients	0.8144–1.1239
No. parameters refined (n_v)	326
R	0.038
R_w	0.058
GOF	2.358

$R = \Sigma(\|F_o| - (1/k)|F_c\|)/\Sigma|F_o|$.

$R_w = [\Sigma w(|F_o| - (1/k)|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ where $w = [\sigma^2(F_o)]^{-1}$; $\sigma(F_o) = [\sigma^2(F_o{}^2) + f^4(F_o{}^2)]^{1/2}/2F_o$ with $f = 0.040$.

$GOF = [\Sigma w(|F_o| - (1/k)|F_c|)^2/(n_o - n_v)]^{1/2}$.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and measured every hour; no significant variation was detected. Data have been corrected for Lorentz and polarization factors using the data reduction programs of the MOLEN crystallographic package [13]. An empirical absorption correction [14] was applied by using azimuth (Ψ) scans of four 'high-χ-angle' reflections ($\chi > 86.5°$; $12.6° < \theta < 23.3°$).

The standard deviations on intensities were calculated in term of statistics alone, while those on F_o were calculated as reported in Table 1.

The structure was solved by a combination of Patterson and Fourier methods and refined by full-matrix least-squares [13]. The function minimized was $(\Sigma w(|F_o| - 1/k|F_c|)^2])$ with $w = [\sigma^2(F_o)]^{-1}$. No extinction correction was found to be necessary. After refining to convergence the complete structural model with isotropic temperature factors for all atoms, a further empirical absorption correction was applied to the data set using the program DIFABS [15].

The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature [16]. Anisotropic temperature factors were used for all atoms. The contribution of the hydrogen atoms in their idealized positions (C–H = 0.95 Å, $B = 5.0$ Å^2) was taken into account but not refined. Upon convergence (no parameter shift > $0.1\sigma(p)$) the final Fourier difference map showed no significant feature. All calculations were carried out using the Enraf-Nonius MOLEN crystallographic programs [13].

Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Description of the structure

The (en)Pd entity is bound to the N3 positions of the two deprotonated 1-methylthymine rings and the two Na^+ are coordinated pairwise by O4 and O2 oxygens (Fig. 1). The usual problem of differentiating O2 and O4 oxygens in 1-MeT unambiguously (pseudo-C_2 axis through N3 and C6), applies also to this compound. In principle, three different arrangements (I–III, Scheme 1) are feasible: a head–head orientation of the two 1-MeT rings (I) and two head–tail orientations (II, III). A complete refinement of all three models does not produce significant differences (R values) among the three models. In particular, there is no systematic trend in the thermal factors that might be used to differentiate between N1 and C5 sites. The atom numbering scheme used in Fig. 1 assumes a head–head orientation of the 1-MeT rings, hence model I. *Cis*-$a_2Pt(1\text{-}MeU)_2$ com-

Table 2
Final positional and equivalent isotropic displacement parameters for the title compound

Atom	x	y	z	B (Å^2)
Pd	0.02038(3)	0.16417(1)	0.28336(2)	1.553(5)
Na1	0.4185(2)	0.17146(8)	0.3878(1)	2.81(3)
Na2	−0.4042(2)	0.13811(9)	0.2051(1)	2.79(3)
O1	1.8231(5)	0.1620(2)	0.0024(3)	4.05(8)
O2a	−0.3051(3)	0.1380(2)	0.3755(2)	2.76(5)
O2	−0.2056(3)	0.0676(2)	0.1674(2)	2.90(6)
O4	0.3461(3)	0.0965(1)	0.2495(2)	2.54(5)
O4a	0.2449(3)	0.1061(2)	0.4539(2)	3.10(6)
O5	0.4371(7)	0.3445(2)	0.5448(3)	6.2(1)
O6	0.2794(5)	0.2680(3)	0.4784(3)	6.7(1)
O7	0.5396(5)	0.2622(2)	0.4824(4)	6.5(1)
O8	0.4368(5)	0.2323(2)	0.2431(3)	4.92(9)
O9	0.6525(6)	0.2817(5)	0.2299(5)	13.8(2)
O10	0.441(1)	0.3330(3)	0.2470(9)	13.4(3)
N1a	−0.2104(4)	0.0868(2)	0.5246(2)	2.77(7)
N1	−0.0332(4)	−0.0147(2)	0.1329(2)	2.63(6)
N2	0.0775(4)	0.2119(2)	0.1637(2)	2.45(6)
N3a	−0.0301(3)	0.1216(2)	0.4108(2)	1.81(5)
N3	0.0689(3)	0.0793(2)	0.2200(2)	1.72(5)
N4	−0.0303(4)	0.2530(2)	0.3326(2)	2.53(6)
N5	0.4169(5)	0.2928(2)	0.5027(3)	4.23(9)
N6	0.5103(5)	0.2847(2)	0.2411(3)	3.84(8)
C1a	−0.3785(5)	0.0819(3)	0.5516(4)	4.2(1)
C1	−0.1741(5)	−0.0541(2)	0.0843(3)	2.93(8)
C2a	−0.1885(4)	0.1169(2)	0.4332(3)	2.04(6)
C2	−0.0632(4)	0.0455(2)	0.1735(3)	1.91(6)
C4a	0.1046(4)	0.0991(2)	0.4735(3)	1.88(6)
C4	0.2298(4)	0.0612(2)	0.2172(3)	1.93(6)
C5	0.2552(4)	0.0019(2)	0.1753(3)	1.85(6)
C5a	0.0782(4)	0.0692(2)	0.5611(2)	1.50(6)
C5a′	0.2224(5)	0.0469(2)	0.6301(3)	2.73(8)
C5′	0.4251(5)	−0.0196(2)	0.1682(4)	3.56(9)
C6	0.1240(5)	−0.0344(2)	0.1356(3)	2.37(7)
C6a	−0.0777(4)	0.0638(2)	0.5838(3)	2.20(7)
C7	0.0329(6)	0.3015(2)	0.2676(3)	3.21(9)
C8	0.0105(6)	0.2776(2)	0.1638(3)	3.05(8)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$.

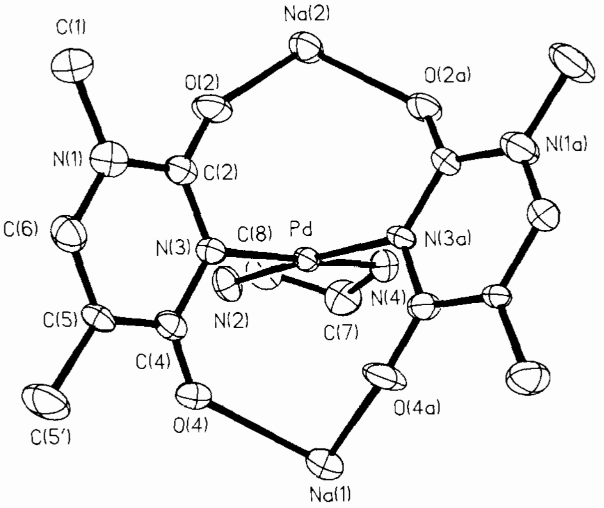
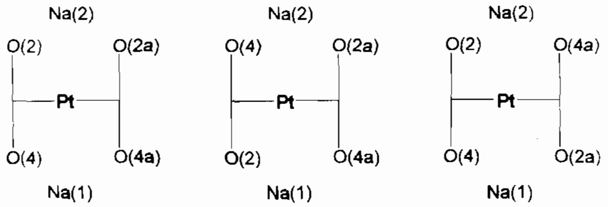


Fig. 1. View of the $[(en)Pd(1\text{-}MeT)Na_2]^{2+}$ cation (**2**) with atom numbering scheme. The head–head orientation of the two 1-MeT rings is assumed on the basis of findings with similar 1-MeU compounds.



I (hh) II (ht) III (ht)

Scheme 1.

pound heterometals thus far have always been found to coordinate successively [1], viz. first at the two O4 sites in a head–head arranged *cis*-$a_2Pt(1\text{-}MeU)_2$ entity and only then at the two O2 sites (cf. also below). Table 3 lists selected interatomic distances and angles and planes and angles are given in Table 4.

Pd has a normal square-planar coordination geometry. Pd–N distances both to the en ligand and to the nucleobase nitrogens are also normal [12,17]. The ethylenediamine chelate adopts a gauche conformation. There are no unusual structural features in the two 1-MeT rings [12]. Specifically, C(2)–O(2) and C(4)–O(4) average bond lengths are 1.238(11) and 1.232(5) Å, respectively. The substituents in the two 1-MeT rings are bent away from the least-squares planes defined by the six atoms in the rings. The dihedral angle between the two 1-MeT rings is 89.4(1)° while the angles between these rings and the coordination plane (defined by atoms Pd, N3, N3a, N2, N4) are 79.0(1) and 72.6°, respectively. The three metals are not exactly colinear but rather form a 170.5(1)° angle at the Pd (Fig. 2).

The trinuclear cations are arranged in polymeric strands, with Na^+ ions acting as bridges between $(en)Pd(1\text{-}MeT)_2$ entities (Fig. 3). Due to the *cis*-arrangement of the nucleobases around Pd, the polymeric strands look like long clefts. The polymeric arrangement, as seen in the title compound, has some similarity with that of *trans*-$[(NH_3)_2Pt(1\text{-}MeU)_2Ag_2]^{2+}$ [4] as far as the roles of the exocyclic nucleobase oxygens are concerned. In $PtAg_2$, one of the two oxygens of each nucleobase (O(4)) acts as a bidentate donor for two Ag^+ ions, whereas the second oxygen, O(2), coordinates to a single Ag^+ only. This picture is consistent with all our previous findings of O(4) being more basic than O(2), hence being the better donor. However, assuming a head–head orientation in the title compound **2** (Fig. 1), only one O(4) oxygen, that of 1-MeT (a), bridges two Na^+ ions, whereas the second bridging oxygen is O(2). With the assumption of O(4) and O(4a) oxygens

Table 3
Selected bond lengths (Å), angles and torsion angles (°) for **2**

Pd–N2	2.026(3)	N2–C8	1.480(5)
Pd–N4	2.039(4)	N4–C7	1.488(6)
Pd–N3	2.038(3)	C7–C8	1.488(7)
Pd–N3a	2.049(3)		
N3–C2	1.369(5)	N3a–C2a	1.381(4)
N3–C4	1.378(4)	N3a–C4a	1.378(4)
N1–C2	1.411(5)	N1a–C2a	1.432(5)
N1–C6	1.348(5)	N1a–C6a	1.346(5)
C4–C5	1.394(5)	C4a–C5a	1.393(5)
C5–C6	1.363(5)	C5a–C6a	1.364(5)
O2–C2	1.274(4)	O2a–C2a	1.228(4)
O4–C4	1.235(4)	O4a–C4a	1.228(4)
N1–C1	1.494(5)	N1a–C1a	1.481(5)
C5–C5′	1.481(5)	C5a–C5′a	1.477(5)
N2–Pd–N3a	175.7(1)	Pd–N3–C4	119.8(2)
N3–Pd–N4	174.1(1)	Pd–N3a–C4a	115.6(2)
N2–Pd–N3	90.3(1)		
N3a–Pd–N4	92.3(1)		
N2–Pd–N4	84.2(1)		
N3–Pd–N3a	93.3(1)		
C2–N3–C4	122.9(3)	C2a–N3a–C4a	122.3(3)
N3–C2–N1	118.0(3)	N3a–C2a–N1a	117.7(3)
C2–N1–C6	118.8(3)	C2a–N1a–C6a	119.1(3)
N1–C6–C5	122.5(4)	N1a–C6a–C5a	122.5(3)
C4–C5–C6	120.1(3)	C4a–C5a–C6a	120.0(3)
N3–C4–C5	117.1(3)	N3a–C4a–C5a	118.4(3)
N3–C2–O2	120.7(3)	N3a–C2a–O2a	120.2(3)
N1–C2–O2	121.2(3)	N1a–C2a–O2a	122.1(3)
N3–C4–O4	121.4(3)	N3a–C4a–O4a	121.1(3)
C5–C4–O4	121.5(3)	C5a–C4a–O4a	120.5(3)
C2–N1–C1	119.9(3)	C2a–N1a–C1a	119.1(3)
C6–N1–C1	121.2(4)	C6a–N1a–C1a	121.8(4)
C4–C5–C5′	119.6(3)	C4a–C5a–C5′a	118.6(3)
C6–C5–C5′	120.1(4)	C6a–C5a–C5′a	121.3(3)
Pd–N4–C7–C8	36.0(4)	N2–Pd–N4–C7	−11.3(3)
Pd–N2–C8–C7	39.1(3)	N4–Pd–N2–C8	−15.3(3)
N4–Pd–N3–C4	94.0(1.2)	N2–C8–C7–N4	−49.9(4)
N2–Pd–N3a–C4a	−71.6(1.7)		

Table 4
Selected contacts (Å) and angles (°) involving the Na ions

Na1–Na2^{*a}	3.141(2)	Na2–O2	2.309(3)
Na1–O2a^{*a}	2.402(3)	Na2–O2a	2.349(3)
Na1–O4	2.458(3)	Na2–O4^{*b}	2.383(3)
Na1–O4a	2.255(3)	Na2–O5^{*c}	2.404(4)
Na1–O6	2.704(6)	Na2–O8	2.460(5)
Na1–O7	2.425(5)	Na2–O9^{*b}	3.050(10)
Na1–O8	2.371(4)		
O2a^{*a}–Na1–O4	83.4(1)	O2–Na2–O2a	93.7(1)
O2a^{*a}–Na1–O4a	120.6(1)	O2–Na2–O5^{*c}	101.6(2)
O2a^{*a}–Na1–O7	87.0(1)	O2a–Na2–O8*	84.8(1)
O2a^{*a}–Na1–O8	85.6(1)	O8^{*c}–Na2–O5^{*b}	80.6(2)
O4–Na1–O4a	79.9(1)	O4^{*b}–Na2–O2a	86.2(1)
O4–Na1–O8	75.0(1)	O4^{*a}–Na2–O8^{*a}	74.7(1)
O4a–Na1–O7	119.7(2)	O4^{*a}–Na2–O5^{*c}	85.1(2)
O7–Na1–O8	87.3(1)	O4^{*b}–Na2–O2	118.9(1)
O6–Na1–O4	139.1(1)	O9^{*b}–Na2–O2	123.5(1)
O6–Na1–O4a	86.4(1)	O9^{*a}–Na2–O2a	82.3(1)
O6–Na1–O7	48.7(1)	O9^{*c}–Na2–O5^{*b}	90.3(2)
O6–Na1–O8	93.5(1)	O9^{*b}–Na2–O8^{*b}	42.7(1)
O4–Na1–O7	160.4(2)	O2a–Na2–O5^{*c}	164.6(2)
O4a–Na1–O8	141.1(1)	O2–Na2–O8^{*b}	166.2(1)
O2a^{*a}–Na1–O6	135.6(1)	O4^{*a}–Na2–O9^{*b}	117.0(1)

Starred atoms are obtained by the following symmetry operations: $^{a}1+x, y, z$; $^{b}1-x, y, z$; $^{c}-1+x, \frac{1}{2}+y, -\frac{1}{2}+z$.

acting as bridging ligands in both cases, a head–tail arrangement of the two 1-MeT ligands (model II, O(2) and O(4) in Fig. 2 interchanged) would indeed seem to be more consistent. X-ray crystallography does not give an answer, however.

Regardless of this question, each Na$^+$ is coordinated by three keto oxygens (two intramolecular bonds, one intermolecular bond) and in addition has three contacts to nitrate oxygens (Fig. 4 and Table 4). The coordination polyhedrons about the Na$^+$ ions may therefore be described as highly distorted trigonal prisms. Na–O distances vary strongly, but are not unusual [10,18,19].

Surprisingly, the water molecule (O1) does not take part in the ligation of Na$^+$ but rather is involved in H bonding. Its shortest contact is to O7*, 2.794(6) Å. Pd–Na(1) (3.371(2) Å) and Pd–Na(2) (3.533(2) Å) are too long to imply any substantial metal–metal interaction. A packing diagram of the title compound is given in Fig. 4. Superficially, the packing can be considered as consisting of columns of Na$^+$ ions, which are separated by (en)Pt(1-MeT)$_2$ moieties and joined by nitrate counter ions.

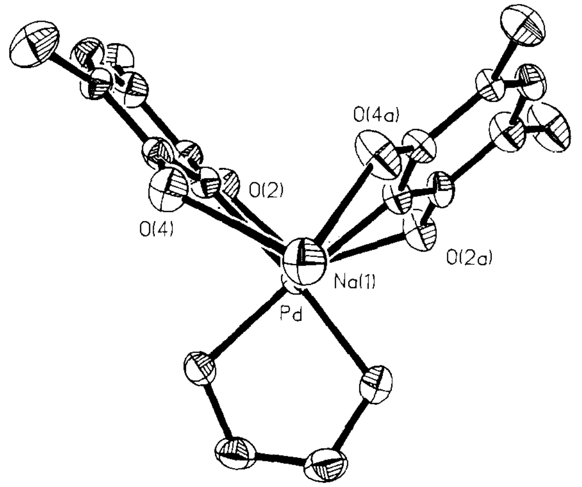


Fig. 2. View along the three metals Na1,Pd,Na2 in **2**. The three metals are not exactly colinear but form an angle of 170.5(1)° at the central Pd.

4. Conclusions

The title compound once more underlines and confirms the excellent ligating properties of compounds of general formula *cis*-a_2ML_2 ($a = NH_3$ or a_2 = diamine; $M = Pt^{II}$ or Pd^{II}) via the exocyclic oxygens of the py-

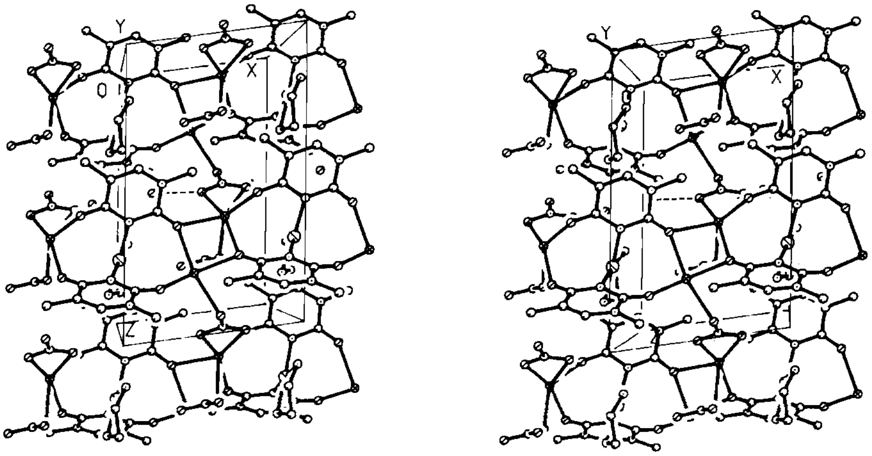


Fig. 3. Section of polymeric strand of cations of 2 with the atom numbering scheme used in Fig. 1. If O(4) and O(2) were to be interchanged (model II), both O(4) and (O4a) would bridge two Na^+ ions whereas O(2) and O(2a) would bind to a single Na^+ ion each.

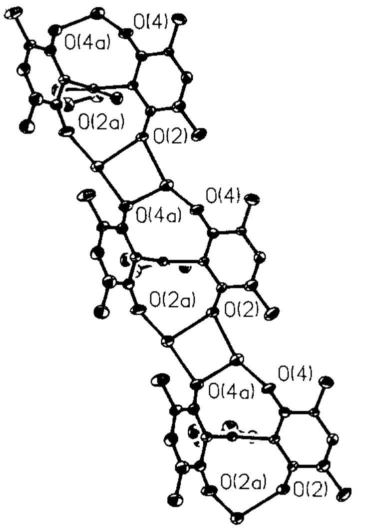


Fig. 4. Stereoview of the packing of 2. The view is along the *y* axis.

rimidine nucleobases L. The here described heteronuclear compound of *cis*-$[a_2ML_2M'_2]^{2+}$ stoichiometry combines soft ($M = Pd^{II}$) and hard ($M' = Na^I$) metals and completes the list of stoichiometry of heteronuclear complexes derived from *cis*-a_2ML_2 [1,2]. As far as binding of hard alkali ions to nucleobases is concerned, this finding as well as related ones with the soft CH_3Hg^+ [10], Pt^{II} [11] and Au^{III} [18] adds further support to a proposal [10] that a synergy of binding of soft and hard metal ions to natural nucleic acids might exist and be biologically relevant.

5. Supplementary material

Tables of anisotropic displacement parameters, of least-squares planes and a list of calculated and observed structure factors may be obtained from the authors upon request.

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References

[1] B. Lippert, *Prog. Inorg. Chem., 37* (1989) 1.

[2] (a) B. Lippert, in J.R. Lusty (ed.), *Handbook of Nucleobase Complexes,* Vol. I, CRC, Boca Raton, FL, 1990, pp. 9–46; (b) B. Lippert, in M.F. Gielen (ed.), *Metal-Based Anti-Tumour Drugs,* Freund, London, 1988, pp. 201–233.

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

[4] (a) H. Schöllhorn, U. Thewalt and B. Lippert, *J. Chem. Soc., Chem. Commun.,* (1984) 769; (b) I. Dieter, B. Lippert, H. Schöllhorn and U. Thewalt, *Z. Naturforsch., Teil B, 45* (1990) 731.

[5] B. Lippert, U. Thewalt, H. Schöllhorn, D.M.L. Goodgame and R.W. Rollins, *Inorg. Chem., 23* (1984) 2807.

[6] H. Schöllhorn, U. Thewalt and B. Lippert, *Inorg. Chim. Acta, 135* (1987) 155.

[7] M. Krumm, B. Lippert, L. Randaccio and E. Zangrando, *J. Am. Chem. Soc., 113* (1991) 5129.

[8] D. Neugebauer and B. Lippert, *J. Am. Chem. Soc., 104* (1982) 6596.

[9] G. Frommer, F. Lianza, A. Albinati and B. Lippert, *Inorg. Chem., 31* (1992) 2434.

[10] F. Guay and A. Beauchamp, *Inorg. Chim. Acta, 66* (1982) 57.

[11] O. Renn, B. Lippert and I. Mutikainen, *Inorg. Chim. Acta, 218* (1994) 117.

[12] (a) W. Micklitz, W.S. Sheldrick and B. Lippert, *Inorg. Chem., 29* (1990) 211. (b) O. Renn, B. Lippert, F. Lianza and A. Albinati, *Inorg. Chim. Acta, 211* (1993) 177.

[13] *MOLEN: Molecular Structure Solution Procedure,* Enraf Nonius, Delft, Netherlands, 1990.

[14] A.C.T. North, D.C. Phillips and F.S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.
[15] N. Walker and D. Stuart, *Acta Crystallogr., Sect A, 39* (1983) 159.
[16] *International Table for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974.
[17] W. Micklitz, J. Riede, B. Huber, G. Müller and B. Lippert, *Inorg. Chem., 27* (1988) 1979.
[18] B. Fischer, H. Preut, B. Lippert, H. Schöllhorn and U. Thewalt, *Polyhedron, 9* (1990) 2199.
[19] N.S. Poonia and A.V. Bajaj, *Chem. Rev., 79* (1979) 389.