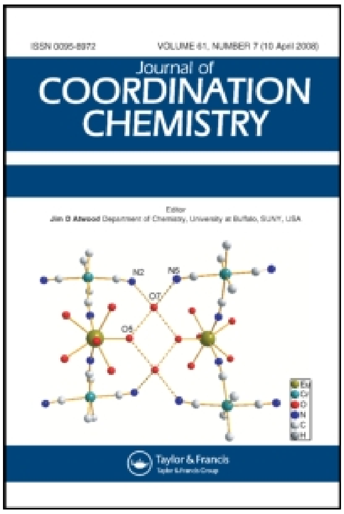

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Crystal structures of complexes of 3,5,6-tris(2-pyridyl)-1,2,4-triazine: $[Pb(TPT)(NO_3)_2]_n$ and $[Pb(TPT)_2(ClO_4)(H_2O)] \cdot ClO_4 \cdot H_2O$

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Two new Pb(II) complexes, $[Pb(TPT)(NO_3)_2]_n$ (**1**) and $[Pb(TPT)_2(ClO_4)(H_2O)] \cdot ClO_4 \cdot H_2O$ (**2**) (TPT is the abbreviation of 3,5,6-tris(2-pyridyl)-1,2,4-triazine), have been synthesized and characterized by single-crystal X-ray diffraction. Lead(II) in the compounds of **1** and **2** is nine coordinate (rare mode), PbN_3O_6 and PbN_6O_3, respectively. Both have hemidirected coordination geometries. The supramolecular features in these complexes are guided/controlled by hydrogen bonding and weak directional intermolecular C–H $\cdots$ O and $\pi \cdots \pi$ interactions. The thermal stabilities of **1** and **2** were investigated by thermogravimetric measurements.

Keywords: Lead(II); 1,2,4-Triazine; Crystal structure

1. Introduction

Supramolecular structures have manifold coordination modes, intriguing architecture, and porosity; and physicochemical characteristics and potential applications as functional materials [1]. Self-assembly has the possibility of rationally designing and synthesizing supramolecular architectures based on covalent or supramolecular contacts [1g]. In crystal engineering, synergistic effects between intermolecular non-covalent interactions must be regarded as a single inter-related entity [2]. Creation of high-dimensional supramolecular architectures can be accomplished by employing coordination bonds, hydrogen bonds, aromatic $\pi \cdots \pi$ stacking interactions, etc. The 3,5,6-tris(2-pyridyl)-1,2,4-triazine (TPT) ligand may also be a very good candidate because of its aromatic rings and ability for forming intermolecular C–H $\cdots$ O and $\pi \cdots \pi$ weak interactions with neighboring ligands.

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2. Experimental

2.1. *Preparation of $[Pb(TPT)(NO_3)_2]_n$ (1) and $[Pb(TPT)_2(ClO_4)(H_2O)] \cdot ClO_4 \cdot H_2O$ (2)*

The titled complexes were prepared by the branched tube method: TPT (0.312 g, 1 mmol) was placed in one arm of the branched tube and lead(II) nitrate (0.331 g, 1 mmol) or lead(II) perchlorate trihydrate (0.230 g, 0.5 mmol) in the other one. Methanol was then carefully added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at 60°C, while the other was left at ambient temperature. After 4 days, crystals deposited in the arm at ambient temperature were filtered off, washed with acetone and ether, and dried in air. For **1** m.p.: 260°C, yield: 40% and for **2** m.p.: 222°C, yield: 50%. Elemental analysis: Calcd for $C_{18}H_{12}N_8O_6Pb$ **1**: C: 33.56, H: 1.86, N: 17.40, found: C: 33.40, H: 1.70, N: 17.00% and for $C_{36}H_{28}Cl_2N_{12}O_{10}Pb$ **2**: C: 40.49, H: 3.15, N: 15.75, found: C: 40.40, H: 2.90, N: 15.40%.

2.2. *Crystallography*

Crystallographic data were collected at 100.0(1) K with the Oxford Cyrosystem Cobra low-temperature attachment. The data were collected using a Bruker Apex2 CCD diffractometer with a graphite monochromated Mo-Kα radiation at a detector distance of 5 cm with APEX2 software [3]. The collected data were reduced using SAINT, and the empirical absorption corrections were performed using SADABS [3]. The structures were solved by direct methods and refined by least-squares using the SHELXTL software package [4]. Materials for publication were prepared using SHELXTL [4] and ORTEPIII [5].

3. Results and discussion

Determination of the structures of $[Pb(TPT)(NO_3)_2]_n$ (**1**) and $[Pb(TPT)_2(ClO_4)(H_2O)] \cdot ClO_4 \cdot H_2O$ (**2**) by X-ray crystallography (table 1) showed a 1D coordination polymer and monomer, respectively. Similar to the recent lead(II) complex [6], coordination of lead(II) is nine in **1**, with each lead chelated by three nitrogens of "TPT" with Pb–N distances of 2.549(2), 2.654(2), and 2.692(2) Å, and six oxygens of nitrates with Pb–O distance of 2.489(2), 2.651(2), 2.774(2), 2.817(2), 2.826(3), and 2.982(2) Å (figure 1, table 2). In the present zig-zag 1D coordination polymer only one nitrate does not bridge between two lead centers. It rather chelates to just one lead center (figure 1) [7].

The coordination number of lead(II) is nine in **2** (figure 2) and each lead is chelated by six nitrogens of "TPT" with Pb–N distances of 2.573(4), 2.663(4), 2.683(4), 2.710(4), 2.763(5), and 2.788(5) Å, two oxygens of perchlorate with a Pb–O distance of 2.995(4) and 3.045(4) Å, and one water with a Pb–OW distance of 2.709(4) Å (table 2). The other, disordered water and disordered perchlorate do not participate in coordination. Two $[Pb(TPT)_2(H_2O)] \cdot H_2O$ are bridged into a centro-symmetric dimer by strong hydrogen bonding between water and nitrogens of triazine

Table 1. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{18}H_{12}N_8O_6Pb$	$C_{36}H_{28}Cl_2N_{12}O_{10}Pb$
Formula weight	643.55	1066.79
Temperature (K)	100.0(1)	100.0(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pca21*	*P21/n*
Unit cell dimensions (Å, °)		
a	17.3753(4)	10.0992(1)
b	15.5977(3)	14.1018(2)
c	7.2248(2)	27.8916(3)
α	90.00	90.00
β	90.00	90.411(1)
γ	90.00	90.00
Volume	1958.03(8)	3972.13(8)
Z	4	4
Density (Calcd)	2.183	1.784
Absorption coefficient	8.675	4.456
$F(000)$	1224	2096
Crystal size (mm^3)	0.51 × 0.16 × 0.14	0.23 × 0.17 × 0.07
θ range for data collection (°)	2.34–40.00	2.48–30.14
Index ranges	$-30 \le h \le 31$	$-12 \le h \le 14$
	$-28 \le k \le 27$	$-19 \le k \le 19$
	$-12 \le l \le 12$	$-39 \le l \le 36$
Reflections collected	77490	95479
Independent reflections	9797[R(int) = 0.0479]	11713[R(int) = 0.0666]
Completeness to θ	99.5	98.8
Full-matrix least squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	11892/1/298	11713/0/578
Maximum and minimum transmission	0.2982–0.0515	0.7339–0.4207
Goodness-of-fit on F^2	1.024	1.089
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0298$	$R_1 = 0.0471$
	$wR_2 = 0.0599$	$wR_2 = 0.1067$
R indices (all data)	$R_1 = 0.0428$	$R_1 = 0.0834$
	$wR_2 = 0.0639$	$wR_2 = 0.1262$
Largest difference peak, hole (e Å^{-3})	3.120, −0.689	2.044, −1.193

(N4 ··· O1W, O1W ··· O2W, and O2W ··· N6 with distance of 3.036(6), 2.669(7), and 2.796(8) Å, respectively) (figure 3) [8].

The arrangement of these ligands suggests a gap or hole [9] around Pb^{II} (in **1**, $O4^{i}$–Pb1–N1 angle is 143.63(7)° and in **2** $O3^{i}$–Pb1–O1W angle is 108.33(1)°), occupied possibly by a stereo-active lone pair of electrons on lead(II). Observed shortening of the Pb–O and Pb–N bonds on the side of Pb(II) ion opposite to the putative lone pair (in **1**, 2.489(2) Å compared with 2.982(2) Å adjacent to the lone pair and in **2**, 2.573(4) Å compared with 3.045(4) Å adjacent to the lone pair) supports this interpretation [10].

An interesting feature in **1** is O ··· H–C interactions {(O3 ··· $H13a^{i}$–$C13a^{i}$ with distance of 2.481 Å (H–C ··· O = 3.314(2) Å and ∠O ··· H–C = 149.28°), O2 ··· $H17a^{i}$–$C17a^{i}$ with distances of 2.441 Å (H–C ··· O = 3.343(1) Å and ∠O ··· H–C = 163.19°) and O4 ··· $H13a^{i}$–$C13a^{i}$ with distances of 2.493(2) Å (H–C ··· O = 3.040(2) Å and ∠O ··· H–C = 117.78°)}, values that suggest relatively strong interactions within this class of weak contacts [11]. The packing diagram exhibits interesting self-assembled structural topologies via two different π–π stackings (face-to-face with distance of 3.357 and edge-to-edge with distance of 3.226 Å, appreciably shorter than the normal

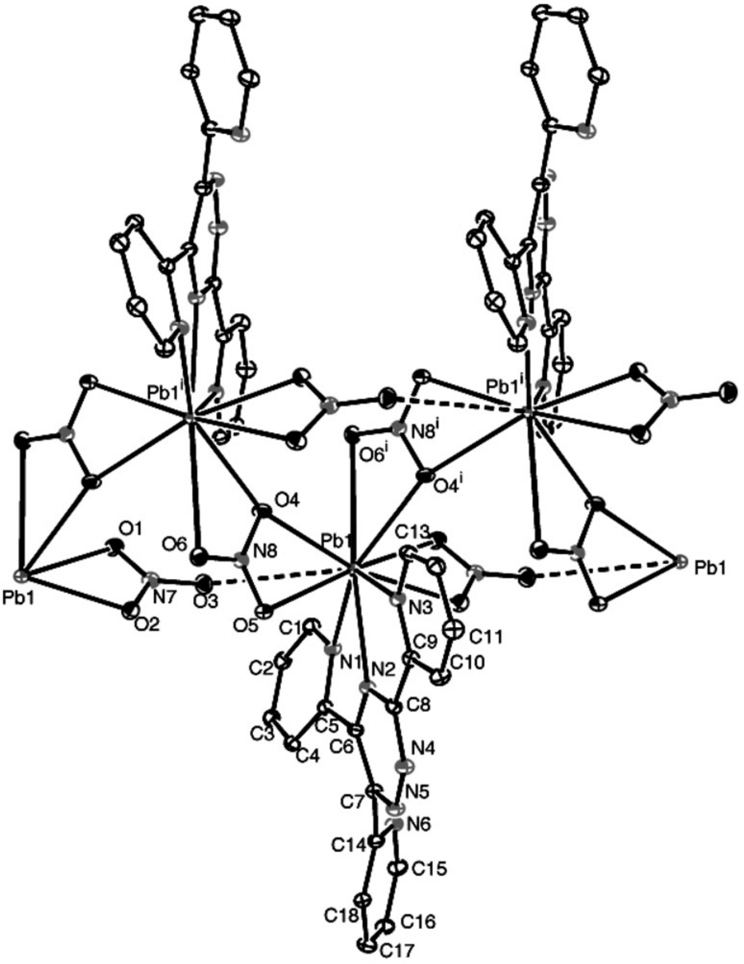

Figure 1. ORTEP diagram of **1** (hydrogen atoms deleted for clarity).

intermolecular interactions) [12]. These weak interactions lead to formation of a 3D framework (figure 4).

The packing diagram of **2** exhibits a 3D supramolecular architecture arising from lone pair activity, π–π stacking and weak $O \cdots H–C$ interaction. It exhibits two different π–π stacking (face-to-face with a distance of 3.368 Å and slipped face-to-face with a distance of 3.291 Å), appreciably shorter than the normal π–π stacking [10]. The 3D framework is stabilized by weak non-covalent $O \cdots H–C$ interaction [13] $\{(O6a \cdots H27a^{iii}\text{-}C27^{iii}$ (iii: $x+1/2, -y+1/2, z+1/2$) with distance of 2.320 Å ($H–C \cdots O = 2.988(2)$ Å and $\angle O \cdots H–C = 128.36^\circ$), $O8a \cdots H3a^{ii}–C3^{ii}$ (ii: $-x, -y, -z$) with distance of 2.333 Å ($H–C \cdots O = 3.200(2)$ Å and $\angle O \cdots H–C = 155.04^\circ$) and $O5 \cdots H19a–C19$ with distances of 2.430 Å ($H–C \cdots O = 3.222(2)$ Å and $\angle O \cdots H–C = 143.02^\circ$)$\}$ (figure 5).

To investigate the stability of these frameworks, thermogravimetric analysis (TGA) was carried out on crystalline samples. For **2**, an initial weight loss of 1.7% (below 120°C) is attributed to loss of the water molecules (Calcd 1.5%). The results show that

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Pb1–O2	2.489(2)	Pb1–N1	2.573(4)
Pb1–N3	2.549(2)	Pb1–N7	2.663(4)
Pb1–O4^{i}	2.651(2)	Pb1–N8	2.683(4)
Pb1–N2	2.654(2)	Pb1–O1W	2.709(4)
Pb1–N1	2.692(2)	Pb1–N2	2.710(4)
Pb1–O5	2.774(2)	Pb1–N9	2.763(5)
Pb1–O4	2.817(2)	Pb1–N3	2.788(5)
Pb1–O1	2.826(3)	Pb1–O4^{i}	2.995(4)
Pb1–O6^{i}	2.982(2)	Pb1–O3^{i}	3.045(4)
Pb1···O3	3.545(3)		
		N1–Pb1–N8	82.92(1)
O2–Pb1–O4^{i}	74.32(7)	N1–Pb1–O1W	77.08(1)
O2–Pb1–N2	68.17(7)	N7–Pb1–O1W	142.64(1)
O4^{i}–Pb1–N2	129.19(7)	N8–Pb1–O1W	134.08(1)
O2–Pb1–N	180.39(7)	N7–Pb1–N2	82.15(1)
O4^{i}–Pb1–N1	143.63(7)	N8–Pb1–N2	136.16(1)
O2–Pb1–N5	138.84(9)	O1W–Pb1–N2	65.74(1)
O2–Pb1–N4	118.28(8)	N1–Pb1–N9	84.22(1)
		O1W–Pb1–N9	77.16(1)
		N2–Pb1–N9	133.95(1)
		N7–Pb1–N3	96.08(2)
		N8–Pb1–N3	140.95(2)
		O1W–Pb1–N3	83.87(2)

i: $-x, -y, z + ½$; ii: $-x + 1/2, y + 1/2, -z + 1/2$.

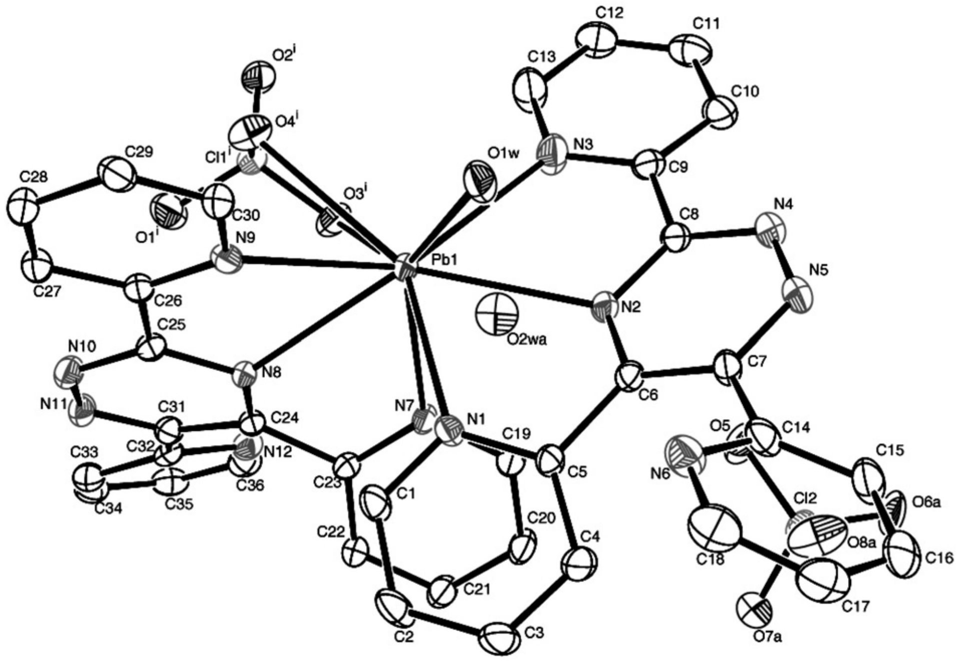

Figure 2. ORTEP diagram of **2** (hydrogen and disorder atoms deleted for clarity).

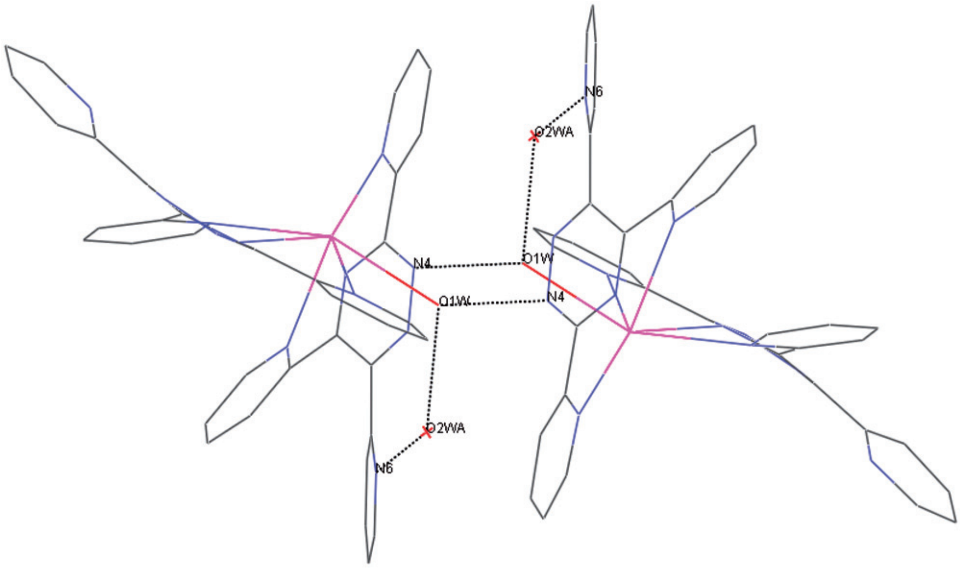

Figure 3. Schematic role of hydrogen bonding in forming dinuclear compound (perchlorate anions deleted for clarity).

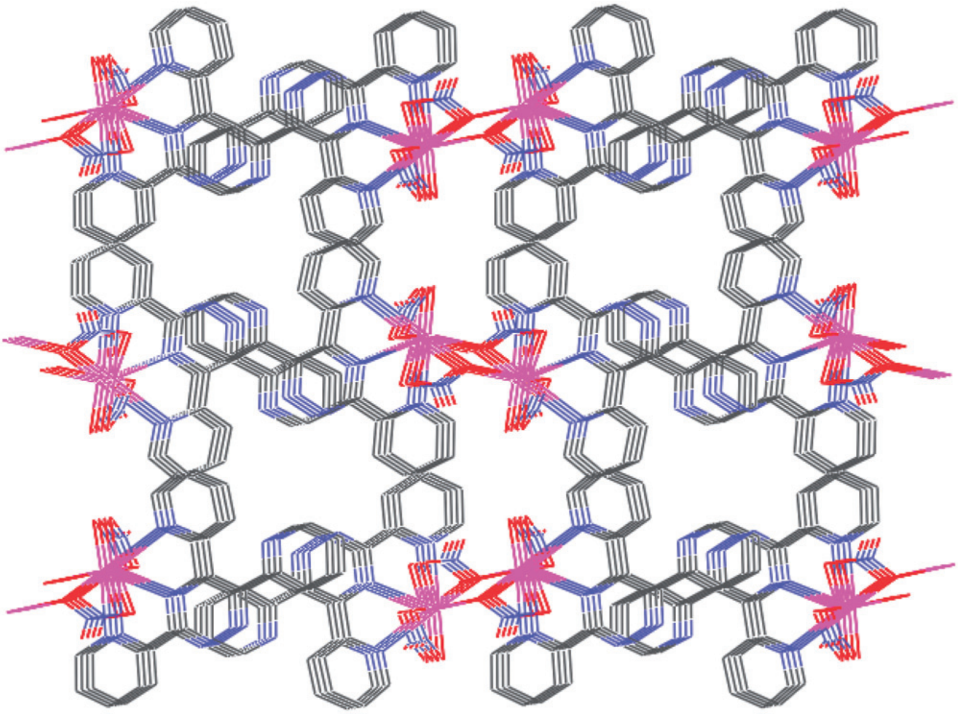

Figure 4. A fragment of 3D framework of **1**.

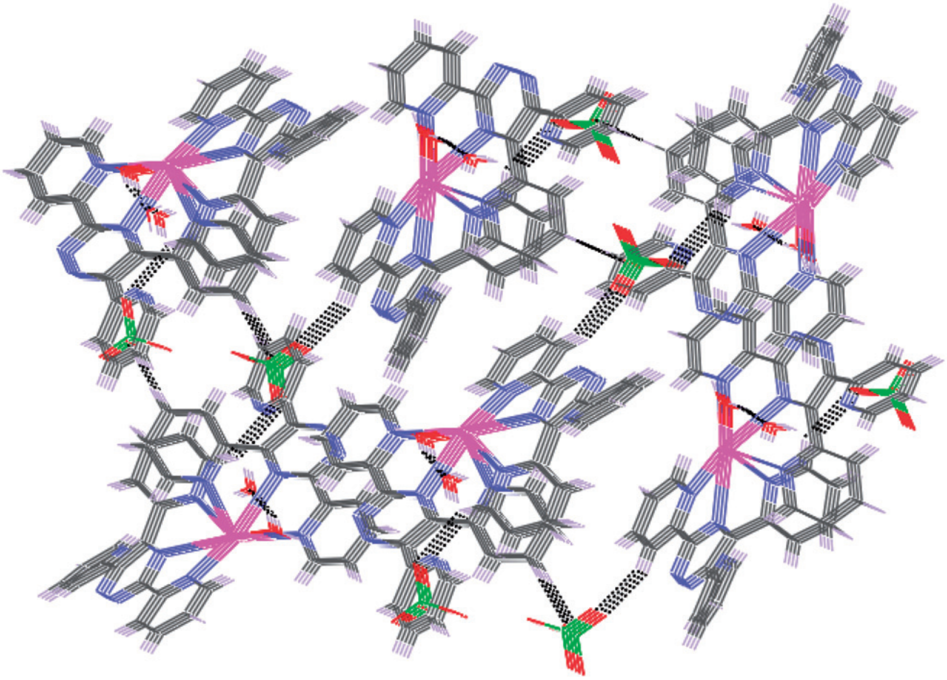

Figure 5. A fragment of 3D framework of **2**.

both compounds almost have similar thermal behavior. The TGA curves of **1** and **2** show that thermal decomposition involves three exothermic processes. Exothermic weight loss occurred between 280 and 600°C (corresponding to loss of "TPT" and decomposition of counter anions). A gray amorphous residue of PbO (observed: 32.32% and 19.5%; Calcd 34.1% and 20.0% for **1** and **2**, respectively) remained. The exothermic DTA peaks of thermal decomposition are due to breaking of these directed intermolecular interactions involved in packing of structures.

Supplementary material

Full crystallographic data, in CIF format, may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44 1223 336 033, by citing deposition numbers 692964 for **1** and 692965 for **2**.

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