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Syntheses and Crystal Structures of the First Zinc Complex with 1,3,5-Triaza-7-phosphaadamantane (PTA), [$ZnCl_2(PTA)_2$], and of the Hybrid Organic–Inorganic Salts of *N*-Methyl-1,3,5-triaza-7-phosphaadamantane with Tetrahalozinc [PTA–Me]$_2$[ZnI_2X_2] (X = I, Cl)

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The Zn^{II} compounds [$ZnCl_2(PTA)_2$] (**1**) (PTA = 1,3,5-triaza-7-phosphaadamantane) and [PTA–Me]$_2$[ZnI_2X_2] [X = Cl (**2a**), X = I (**2b**); PTA–Me = *N*-methyl-1,3,5-triaza-7-phosphaadamantane] have been prepared by treating $ZnCl_2$ with PTA and [PTA–Me]I, respectively, in methanol at room temperature. They are soluble in polar solvents such as water and methanol, stable in air, and have been characterized by IR, ^1H NMR, $^{31}P\{^1H\}$ NMR, and $^{13}C\{^1H\}$ NMR spectroscopy, ESI-MS, elemental and single-crystal X-ray diffraction structural analyses (for **1** and **2a**). Compound **1** exhibits a nearly regular tetrahedral Zn coordination, with the PTA ligands displaying the uncommon *N*-coordination with a low ^{31}P NMR coordination shift. The molecular structure of **2a** bears one discrete tetrahedral [ZnI_2Cl_2]$^{2-}$ anion and two cage-like [PTA–Me]$^+$ cations, one of them being located in a void. Compound **1** represents the first example of a Zn complex bearing PTA or any derived ligand with a cage-like PTA core.

Introduction

The coordination chemistry of PTA has experienced increasing interest over the last years mainly justified by the search for water-soluble phosphane–transition metal complexes.[1,2] These were shown to possess good solubility in aqueous media, therefore leading to several applications either as catalysts in an aqueous phase,[2–5] water-soluble antitumor agents[2,6–8] or photoluminescent materials.[2,9,10] In fact, some of us have previously shown that Rh– and Ru–PTA (and *N*-alkylated PTA) complexes can act as efficient catalysts for the hydrogenation, hydroformylation and isomerization of alkenes in aqueous systems.[1,11,12]

We have recently reported new Re,[13] Cu,[14] Co,[15a] Pt[16] and Rh[17] phosphorus-coordinated PTA complexes, hybrid organic–inorganic Co salts of the type [PTA–R]$_2$[Co(NCS)$_4$] (R = Me, Et),[15b] as well as the *N*-coordinated Co–PTA oxide (PTA=O) compound *trans*-[Co(NCS)$_2$(PTA=O)$_2$(H$_2$O)$_2$].[15a] PTA usually displays the *P*-coordination mode, but scant examples of the other less common ligation modes are known, in particular, the *N*-coordinated PTA complex [$MnX_2(H_2O)_2(PTA)_2$] (X = Cl, Br),[18a] the *P*,*N*-coordinated PTA polymer [CpRu(L)(μ^2-*P*,*N*-PTA)$_2$AgCl$_2$]$_n$ (L = dmso, H_2O)[18b] and the silver(I) coordination polymer containing the bridging tridentate *P*,*N*,*N′*-coordination mode [Ag(μ^2-*P*,*N*,*N′*-PTA)(H$_2$O)]$_n$NO$_3$.[19] The attempt to extend the number of PTA complexes with the uncommon *N*-coordination mode was one of the aims of the present study; such a possibility was tested with a late group metal ion with a strong Lewis and hard acid character, for which no example of a PTA complex had yet been reported.

Moreover, typically zinc is an element of strong interest in biology, medicine, materials and catalysis, and its detection in biological systems can be considerably enhanced by the use of properly designed ligands.[20] A number of zinc complexes with phosphane ligands can be found in the literature, e.g. [$ZnI_2(PR_3)_2$] (PR_3 = PPh_3, PPh_2Et and PPh_2Me) and [$ZnI_2(PR_3)_2$]$_2$ (R = Me, Et, *n*Pr and *n*Bu) synthesized from zinc powder and R_3PI_2,[21] [$ZnCl_2(PMe_3)_2$] and [$(PMe_3)_3Zn(\mu\text{-}Cl)ZnCl_3$], obtained from $ZnCl_2$ and PMe_3.[22] However, all these (tertiary phosphane)zinc(II) complexes are moisture-sensitive, and in order to overcome this stability problem we have now used the hydrosoluble tertiary 1,3,5-triaza-7-phosphaadamantanes PTA and PTA–Me$^+$ instead of the previously applied phosphanes.

We now report on the synthesis of the new, water-soluble Zn^{II} compound [$ZnCl_2(PTA)_2$] (**1**) as well as of the salts [PTA–Me]$_2$[ZnI_2X_2] [X = Cl (**2a**), I (**2b**)]. Compound **1** constitutes, as far as we are aware of, the first isolated example

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of a zinc complex bearing a PTA ligand, which binds the metal atom by the unusual *N*-coordination mode. It can thus be considered as an analogue of the previously described hexamethylenetetraamine (HTM) complex $[ZnI_2(HMT)_2]$.[23] The new compounds were characterized by IR, ^1H NMR, $^{13}C\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR spectroscopy, ESI-MS, elemental and (for **1** and **2a**) single-crystal X-ray diffraction structural analyses.

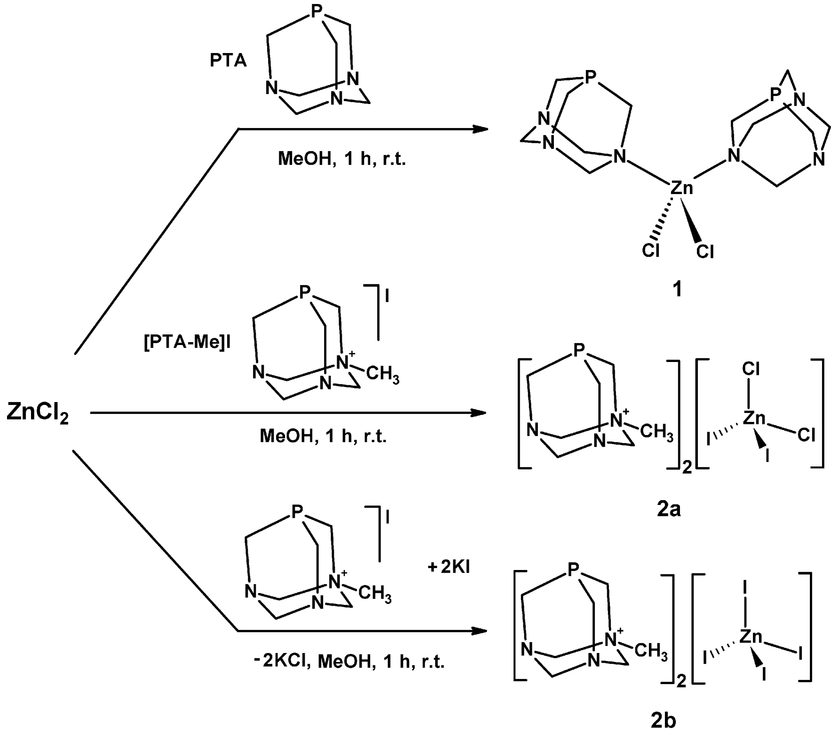
Results and Discussion

Synthesis and Spectroscopic Characterization

Treatment of a methanolic solution of $ZnCl_2$ with PTA or [PTA–Me]I, in the stoichiometric 1:2 molar ratio at room temperature affords (Scheme 1) $[ZnCl_2(PTA)_2]$ (**1**) or the hybrid organic–inorganic salt $[PTA–Me]_2[ZnCl_2I_2]$ (**2a**), respectively, whereas $[PTA–Me]_2[ZnI_4]$ (**2b**) is formed in the presence of an excess of KI. These products were isolated, after a reaction time of 1 h, as white microcrystalline solids in ca. 50–75% yields based on $ZnCl_2$, and characterized by IR and NMR spectroscopy, ESI-MS, elemental and (for **1** and **2a**) single-crystal X-ray diffraction structural analyses. They are air-stable in the solid state and in an aqueous or methanolic solution. They are soluble in H_2O and in other polar solvents, such as MeCN, Me_2SO and $Me_2C(O)NH_2$, sparingly soluble in MeOH and EtOH, and insoluble in other medium- and low-polarity solvents and in non-polar ones such as Me_2CO, *n*PrOH, CH_2Cl_2, $CHCl_3$, Et_2O, CCl_4 or C_6H_6. Analytically pure, colourless single crystals of **1** and **2a** suitable for X-ray analyses were obtained upon cooling the reaction solutions to +4 °C in air.

The ^1H NMR spectrum of **1** in CD_3OD is suggestive of *N*-coordination of PTA. It shows two types of methylene protons for the coordinated PTA (Figure 1a). One of them, assigned to the P–CH_2–N moiety, occurs as a doublet ($J_{P,H}$ = 9.6 Hz) at δ = 4.06 ppm. This is in contrast with the observed behaviour of the complexes with coordinated PTA through the phosphorus atom, where this resonance appears as a broad singlet[12,13,16,17] or a doublet with a lower coupling constant.[14a] The methylene protons of the N–CH_2–N group display a singlet at δ = 4.69 ppm, whereas for the free PTA or some PTA complexes the observed AB spin system is attributed[13] to the N–CH_{ax}–N and N–CH_{eq}–N protons.

The $^{31}P\{^1H\}$ NMR spectrum of **1** exhibits a broad singlet (Figure 1a) at δ = –93.2 ppm (relative to 85% H_3PO_4) with a low coordination shift ($\Delta\delta = \delta_{complex} - \delta_{phosphane}$ = 5.0 ppm), also in agreement with *N*-coordination. An upfield ^{31}P shift occurs upon addition of an excess of free PTA (Figure 1b and c), without observing a distinct resonance of the free phosphane (a similar behaviour, although less pronounced, is observed in the ^1H NMR spectra), which is consistent with fast exchange of coordinated and free phosphanes. The $^{13}C\{^1H\}$ NMR spectrum shows two doublets at $\delta \approx 72.0$ ($^3J_{P,C}$ = 2.0 Hz) and 48.7 ppm ($^1J_{P,C}$ = 21.6 Hz), assigned to the N*C*H_2N and P*C*H_2N carbon nuclei, respectively. In the ESI^+ mass spectrum of **1** in methanol the ions $[ZnCl(PTA)]^+$ and $[PTA–H]^+$ are observed, whereas in water $[Zn(OH)(PTA)_2]^+$ and $[Zn(H_2O)(PTA)]^{2+}$ are also detected (in addition to the former). This is indicative that, in water and under ESI^+-MS conditions, **1** undergoes partial ligand displacement. However, complex **1** is stable in water, under normal conditions, and the solid obtained upon sol-



Scheme 1. Syntheses of **1** and **2**.

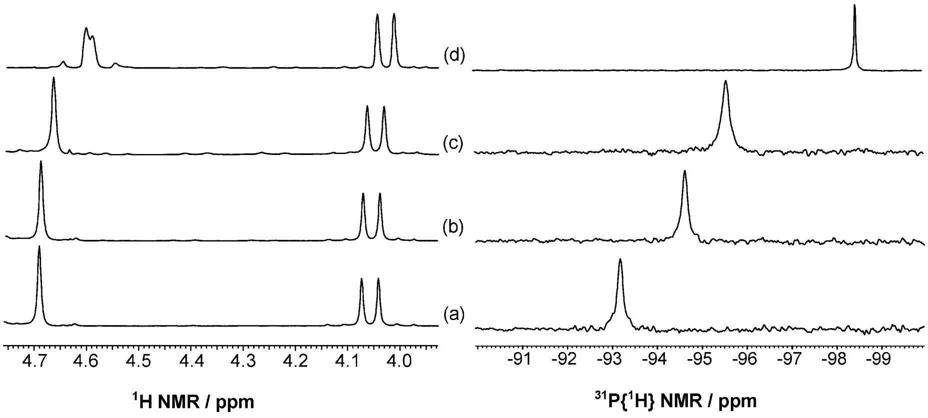


Figure 1. ^{1}H and ^{31}P{^{1}H} NMR spectra of solutions of **1** and/or PTA in CD_3OD; (a) pure solution of **1**; (b), (c) solutions of **1** with an excess of PTA (molar ratio of **1**/PTA = 1:2 and 1:4, respectively); (d) pure solution of free PTA in CD_3OD.

vent evaporation displays IR and ESI$^+$ mass spectra in methanol that are identical to those of the starting solid sample of **1**.

The IR spectrum of **1** (KBr pellet) shows a set of vibrations typical of coordinated PTA, whereas the IR and NMR spectra of **2a** and **2b** are rather similar and display common features from the [PTA–Me]$^+$ moieties. The unshifted character of the latter relative to those of [PTA–Me]-I confirms the uncoordinated nature of [PTA–R]$^+$ in **2a** and **2b**. Similar spectroscopic properties were found for the $[PTA–Me]_2[Co(NCS)_4]$ and $[PTA–Et]_2[Co(NCS)_4]$ salts.[15b] The ESI$^+$ mass spectra of **2a** and **2b** exhibit the molecular ion peak [PTA–Me]$^+$ with the corresponding isotopic distribution, whereas the ESI$^-$ mass spectra show the presence of the anions $[ZnI_2Cl]^-$ and $[ZnICl_2]^-$ (for **2a**) and $[ZnI_3]^-$ (for **2b**).

X-ray Crystal Structures of 1 and 2a

Compound **1** crystallizes in the monoclinic system (space group $P2_1/n$); the asymmetric unit consists of three molecules of the complex, all in general positions. Figure 2 shows an ORTEP drawing of this asymmetric unit with the atom-labelling scheme and the metal-ion environments; pertinent bond lengths and bond angles are given in Table 2.

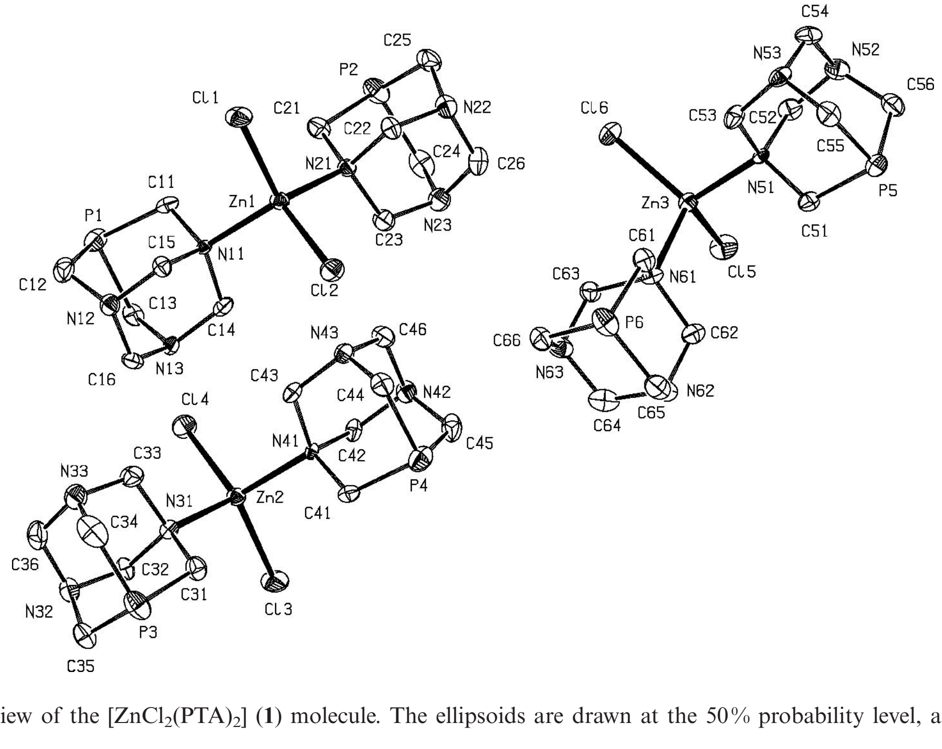


Figure 2. ORTEP view of the $[ZnCl_2(PTA)_2]$ (**1**) molecule. The ellipsoids are drawn at the 50% probability level, and the H atoms are omitted for clarity.

Each of the Zn ions in **1** is located in an approximately tetrahedral geometry that arises in all cases from two chloride ions and two N atoms from independent PTA ligands.

Inspection of the Zn–C–N–P orientations in the molecules of **1** reveals a slight rotation of one of the PTA ligands in the Zn3 molecule (Figure 3). Moreover, significant metrical parameters in the molecule of Zn1 are very similar to those in the molecule of Zn2, whereas that of Zn3 presents the most disparate values (Table 2). Specifically, each of the former two molecules show, unlike the Zn–Cl distances, one being ca. 0.03 Å longer than the other; but in the latter both distances are equivalent. In addition, the Zn3 molecule presents the longest Zn–N distance [2.102(4) Å] and the smallest Cl–Zn–Cl and N–Zn–N angles [113.45(5) and 111.11(13)°, respectively].

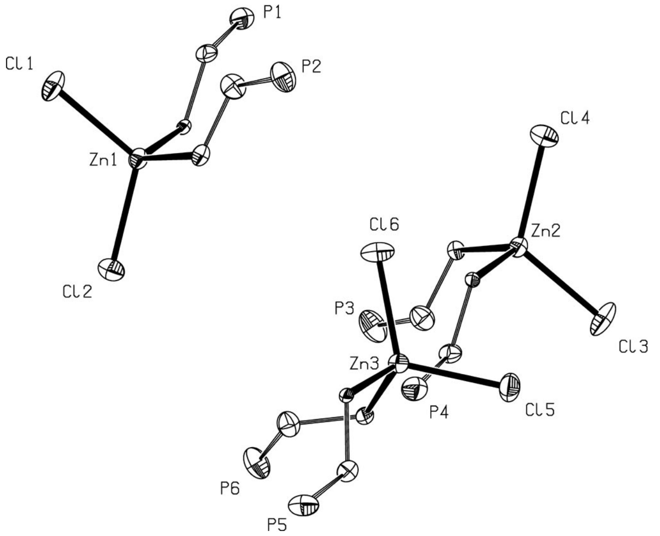


Figure 3. Fragment of the asymmetric unit of **1** showing the relative orientations of the PTA ligands.

The molecular structure of [PTA–Me]$_2$[ZnI$_2$Cl$_2$] (**2a**) (Figure 4) was also authenticated by single-crystal X-ray diffraction analysis, although only one of the PTA–Me cations was found and refined; the remaining one was highly disordered and could not be modelled. On the basis of the number of electrons found in a void, it was considered that this space could accommodate the missing cation. Even with the void treatment[24] the maximum and minimum peaks in the final difference electron density map are 3.427 and –3.707 with no obvious allocations.

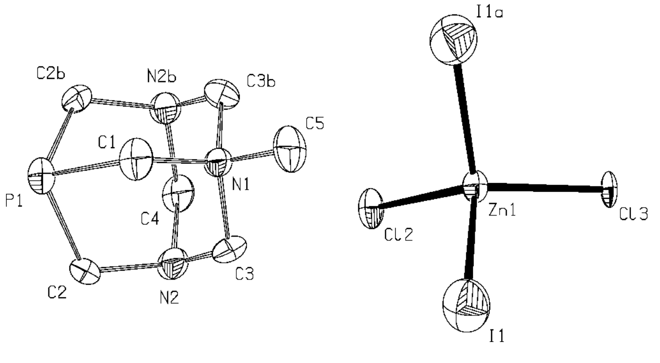


Figure 4. ORTEP view showing the atomic labelling scheme and the metal ion environment in [PTA–Me]$_2$[ZnCl$_2$I$_2$] (**2a**) (50% probability ellipsoids). The second organic cation is located in a void (see text). Codes of equivalent positions: (a), (b): *x*, 1/2 – *y*, *z*. Selected bond lengths [Å]: I1–Zn1 2.5312(14), Zn1–Cl2 2.309(3), Zn1–Cl3 2.294(3); selected angles [°]: I1–Zn1–Cl2 108.10(6), Cl2–Zn1–Cl3 112.78(12), I1–Zn1–Cl3 107.19(6).

Conclusions

The reaction of a dihalozinc compound with 1,3,5-triaza-7-phosphaadamantane (PTA) is a convenient means for the synthesis of an unprecedented Zn^{II} complex with PTA, in which the phosphane ligand displays the unusual *N*-coordination mode rather than the common ligation through the P atom. This is consistent with the effective Lewis and hard acid character of Zn^{2+}, and such properties for this and other late group metals should be further explored to extend the range of *N*-coordinated PTA complexes. The solubility and stability in water of the obtained complex also encourage further developments of this chemistry in aqueous media.

The present work also showed that the decreased coordination ability of the alkylated PTA (i.e. [PTA–Me]$^+$), relative to PTA itself, led to the formation of hybrid organic–inorganic salts of cationic [PTA–Me]$^+$ and anionic tetrahalozinc species [Zn(halo)$_4$]$^{2-}$.

The extension of this study towards the synthesis of Zn^{II} compounds with other PTA derivatives, as well as the search for their catalytic activity in aqueous media, are currently in progress and will be reported elsewhere.

Experimental Section

General: All manipulations were carried out under dry oxygen-free dinitrogen by using standard Schlenk techniques. All solvents were dried, degassed and distilled prior to use. ZnCl$_2$ (Aldrich) was used as received, whereas 1,3,5-triaza-7-phosphaadamantane (PTA)[25] and *N*-methyl-1,3,5-triaza-7-phosphaadamantane iodide [PTA–Me]I[25] were synthesized in accordance with literature methods. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico in Lisbon. Electrospray mass spectra were recorded with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. The solutions in methanol or water were continuously introduced into the mass spectrometer source with a syringe pump at a flow rate of 10 µL/min. The drying gas temperature was maintained at 350 °C, and dinitrogen was used as a nebulizer gas at a pressure of 35 psi. Scanning was performed from *m*/*z* = 50 to 1500. Infrared spectra (4000–400 cm^{-1}) were recorded with a BIO-RAD FTS 3000MX instrument on KBr pellets. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured with a Bruker 300 UltraShieldTM spectrometer at ambient temperatures. ^{1}H and ^{13}C chemical shifts (δ) are expressed in ppm relative to Si(Me)$_4$, and δ(^{31}P) relative to 85% H$_3$PO$_4$. Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; br., broad.

[ZnCl$_2$(PTA)$_2$] (1): A solution (10 mL) of PTA (362 mg, 2.30 mmol) in methanol was added to a methanolic solution (10 mL) of anhydrous ZnCl$_2$ (157 mg, 1.15 mmol) with continuous stirring at room temperature. The resulting white suspension was stirred for 1 h, whereupon the white microcrystalline solid (**1**) was isolated by filtration, washed with cold methanol (3 × 10 mL) and dried in vacuo. Yield 62 % (322 mg), based on zinc chloride. Complex **1** is soluble in H_2O ($S_{25\,°C}$ = 35 mg/mL) and dmso, less soluble in MeOH and EtOH, and insoluble in C_6H_6, $CHCl_3$ and CH_2Cl_2. $C_{12}H_{24}Cl_2N_6P_2Zn$ (450.61): calcd. C 31.98, H 5.37, N 18.65; found C 31.11, H 5.52, N 17.93. ESI^+-MS (CH_3OH): *m*/*z* = 258 $[ZnCl(PTA)]^+$, 158 $[PTAH]^+$. ESI^+-MS (H_2O): *m*/*z* = 397 $[Zn(OH)(PTA)_2]^+$, 258 $[ZnCl(PTA)]^+$, 158 $[PTAH]^+$, 121 $[Zn(H_2O)(PTA)]^{2+}$. ESI^--MS (CH_3OH): *m*/*z* = 172 $[ZnCl_3]^-$. IR (KBr): $\tilde{\nu}$ = 2937, 2930 (s, br.) ν(CH), 1448 (m), 1419 (m), 1303 (m), 1237 (m), 1115 (m), 1025 (s), 960 (s), 919 (s), 888 (m), 818 (m), 759 (s), 617 (w), 560 (s) and 464 (m) (PTA bands) cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 4.69 (s, br., 12 H, NCH_2N), 4.06 (d, $^2J_{P,H}$ = 9.6 Hz, 12 H, PCH_2N) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3OD): δ = 72.0 (d, $^3J_{P,C}$ = 2 Hz, NCH_2N), 48.7 (d, $^1J_{P,C}$ = 21.6 Hz, PCH_2N) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3OD): δ = –93.2 (s, br.) ppm. Single crystals of **1** suitable for X-ray analysis were grown in air from the reaction filtrate at 4 °C for 3 d.

$[PTA–Me]_2[ZnCl_2I_2]$ (2a): A solution (40 mL) of [PTA–Me]I (344 mg, 1.15 mmol) in methanol was added to a methanolic solution (40 mL) of anhydrous $ZnCl_2$ (78.5 mg, 0.575 mmol) with continuous stirring at room temperature. The resulting white suspension was stirred for 1 h, whereafter it was filtered and the solid washed with MeOH (3 × 20 mL) and dried in vacuo to afford **2a** as a white microcrystalline solid. Yield 50 % (212 mg), based on zinc chloride. Compound **2a** is soluble in H_2O and dmso, less soluble in MeOH and EtOH, and insoluble in C_6H_6, $CHCl_3$ and CH_2Cl_2. $C_{14}H_{30}Cl_2I_2N_6P_2Zn$ (734.50): calcd. C 22.89, H 4.12, N 11.44; found C 23.05, H 4.00, N 11.89. ESI^+-MS: *m*/*z* = 172 $[PTA–Me]^+$. ESI^--MS: *m*/*z* = 355 $[ZnI_2Cl]^-$, 263 $[ZnICl_2]^-$. IR (KBr): $\tilde{\nu}$ = 2967, 2952, 2943 (3 s, br.) ν(CH), 1454 (m), 1316 (m), 1248 (s), 1098 (s), 1025 (s), 983 (s), 922 (s), 816 (s), 766 (s), 738 (m), 560 (s) and 444 (PTA–Me bands) cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 4.98 and 4.86 [$J(H^AH^B)$ = 8 Hz, 8 H, $NCH^AH^BN^+$], 4.62 and 4.45 [$J(H^AH^B)$ = 10 Hz, 4 H, NCH^AH^BN], 4.68 (d, $^2J_{P,H}$ = 4.6 Hz 4 H, PCH_2N^+), 4.00 and 3.85 [$J(H^AH^B)$ = 11, $^3J(H^AP)$ = 11, $^3J(H^BP)$ = 6 Hz, 8 H, PCH^AH^BN], 2.68 (s, 6 H, N^+CH_3) ppm. $^{13}C\{^1H\}$ and HMQC ^{13}C-^1H NMR (75.4 MHz, CD_3OD): δ = 80.6 (s, NCH_2N^+), 69.6 (s, NCH_2N), 56.2 (d, $^1J_{P,C}$ = 24 Hz, PCH_2N^+), 48.7 (s, N^+CH_3), 45.7 (d, $^1J_{P,C}$ = 15 Hz, PCH_2N) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3OD): δ = –84.6 (s) ppm. Single crystals of **2a** suitable for X-ray analysis were grown in air, at 4 °C, from the reaction mixture filtrate for two weeks.

$[PTA–Me]_2[ZnI_4]$ (2b): Methanolic solutions (50 mL of each) of anhydrous $ZnCl_2$ (78.5 mg, 0.575 mmol) and [PTA–Me]I (344 mg, 1.15 mmol) were mixed with continuous stirring at ambient temperature. KI (191 mg, 1.15 mmol) was added to the resulting mixture, leading to the gradual precipitation of a white solid, which was completed in 30 min. The obtained suspension was filtered and the solid washed with MeOH (3 × 30 mL) and dried in vacuo to yield compound **2b** as a white microcrystalline solid (397 mg, 75 % yield based on $ZnCl_2$). Compound **2b** is soluble in H_2O and dmso, slightly soluble in MeOH and EtOH, and insoluble in C_6H_6, $CHCl_3$ and CH_2Cl_2. $C_{14}H_{30}I_4N_6P_2Zn$ (917.40): calcd. C 18.33, H 3.30, N 9.16; found C 18.08, H 3.40, N 9.30. ESI^+-MS: *m*/*z* = 172 $[PTA–Me]^+$. ESI^--MS: *m*/*z* = 446 $[ZnI_3]^-$. IR (KBr): $\tilde{\nu}$ = 2966, 2950, 2944 (3 s, br.) ν(CH), 1450 (m), 1312 (m), 1245 (s), 1100 (s), 1029 (s), 983 (s), 920 (s), 815 (s), 750 (s), 562 (s) and 454 (PTA–Me bands) cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 5.00 and 4.88 [$J(H^AH^B)$ = 8 Hz, 8 H, $NCH^AH^BN^+$], 4.63 and 4.46 [$J(H^AH^B)$ = 10 Hz, 4 H, NCH^AH^BN], 4.67 (d, $^2J_{P,H}$ = 4.5 Hz 4 H, PCH_2N^+), 3.98 and 3.80 [$J(H^AH^B)$ = 13, $^3J(H^AP)$ = 10, $^3J(H^BP)$ = 5 Hz, 8 H, PCH^AH^BN], 2.66 (s, 6 H, N^+CH_3) ppm. $^{13}C\{^1H\}$ and HMQC ^{13}C-^1H NMR (75.4 MHz, CD_3OD): δ = 79.9 (s, NCH_2N^+), 68.0 (s, NCH_2N), 58.0 (d, $^1J_{P,C}$ = 22 Hz, PCH_2N^+), 47.6 (s, N^+CH_3), 44.1 (d, $^1J_{P,C}$ = 12 Hz, PCH_2N) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3OD): δ = –84.7 (s) ppm.

Refinement Details for the X-ray Crystal Structure Analyses of 1 and 2a: Intensity data were collected with a Bruker AXS-KAPPA APEX II diffractometer with graphite-monochromated Mo-K_α radiation. Data were collected at 150 K by using ω-scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved by using the Bruker SMART software and refined by using the Bruker SAINT program on all the observed reflections. Absorption corrections were applied by using the SADABS program. Structures were solved by direct methods using the SHELXS-97 package[26] and refined with SHELXL-97 [27] with the WinGX graphical user interface.[28] All hydrogen atoms were inserted in calculated positions. Least-squares refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic parameters for the remaining atoms gave R_1 = 0.0434 [$I > 2\sigma(I)$; R_1 = 0.0732 (all data)] and R_1 = 0.0969 [$I > 2\sigma(I)$; R_1 = 0.1233 (all data)] for **1** and **2a**, respectively. The low diffraction power of **1** justifies the obtained completeness of data (93 %). There is a disorder present in structure **2a** that could not be modelled. The program PLATON/SQUEEZE[28] was used to correct the data. A potential volume of 906.7 Å^3 was found. 422 electrons per unit cell worth of scattering were located in the void. The stoichiometry was calculated as one PTA–Me cation, essential for the balancing of charges in the structure. The crystallographic data are summarized in Table 1, and the selected bond lengths and angles for **1** are given in Table 2. CCDC-703200 and -703201 contain the supplementary crystallographic data of **1** and **2a**, respectively, for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and refinement parameters for **1** and **2a**.

	1	**2a**
Empirical formula	$C_{12}H_{24}Cl_2N_6P_2Zn$	$C_7H_{15}Cl_2I_2N_3PZn$
M_r [g/mol]	450.58	562.26
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	*Pnma*
a [Å]	6.8809(6)	9.2437(9)
b [Å]	35.159(3)	14.480(5)
c [Å]	22.235(2)	17.531(6)
α [°]	90	90
β [°]	90.021(3)	90
γ [°]	90	90
V [Å^3]	5379.3(9)	2346.6(11)
Z′	3	0.75
Z	12	4
$\rho_{calcd.}$ [Mg/m^3]	1.669	1.592
μ(Mo-K_α) [mm^{-1}]	1.853	3.961
F(000)	2784	1052
No. of reflections collected	23042	11506
No. of unique reflections	8800	2743
$R_{int.}$	0.0676	0.0578
Final R_1[a], wR_2[b] ($I \geq 2\sigma$)	0.0434, 0.0837	0.0969, 0.2948
Goodness-of-fit on F^2	0.911	1.116

[a] $R_1 = [\Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for [$ZnCl_2(PTA)_2$] (**1**).

Zn1–Cl1	2.2196 (13)	Zn1–Cl2	2.2461(12)
Zn2–Cl3	2.2131(13)	Zn2–Cl4	2.2415(12)
Zn3–Cl5	2.2342(12)	Zn3–Cl6	2.2313(13)
Zn1–N11	2.055(3)	Zn1–N21	2.089(3)
Zn2–N31	2.080(3)	Zn2–N41	2.059(4)
Zn3–N51	2.070(4)	Zn3–N61	2.101(3)
Cl1–Zn1–Cl2	117.19(5)	N11–Zn1–N21	115.24(13)
Cl3–Zn2–Cl4	117.66(5)	N31–Zn2–N41	114.85(13)
Cl5–Zn3–Cl6	113.45(5)	N51–Zn3–N61	111.12(13)

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