Orthogonal Coordination Chemistry of PTA toward Ru(II) and Zn(II)

The cage-like 1,3,5-triaza-7-phosphaadamantane (PTA, Chart 1), is an amphiphilic, air-stable, neutral ligand of low steric demand (cone angle 103°) characterized by a high solubility in water (ca. 235 g/L). For this reason, PTA and related species—whose coordination chemistry has been thoroughly reviewed by Peruzzini and co-workers—have been largely investigated as supporting ligands for applications in homogeneous aqueous biphasic catalysis and medicinal inorganic chemistry.1–3

PTA typically binds strongly to most transition metal ions through the soft P atom in a monodentate fashion (PTA-xP). However, having also three hard N donor atoms, it is actually a

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ABSTRACT: This work demonstrates that PTA (1,3,5-triaza-7-phosphaadamantane) behaves as an orthogonal ligand between Ru(II) and Zn(II), since it selectively binds through the P atom to ruthenium and through one or more of the N atoms to zinc. This property of PTA was exploited for preparing the two monomeric porphyrin adducts with axially bound PTA, [Ru(TPP)(PTA-xP)] (1, TPP = meso-tetraphenylporphyrin) and [Zn(TPP)(PTA-xP)] (3). Next, we prepared a number of heterobimetallic Ru/Zn porphyrin polymeric networks—and two discrete molecular systems—mediated by P,N-bridging PTA in which either both metals reside inside a porphyrin core, or one metal belongs to a porphyrin, either Ru(TPP) or Zn(TPP), and the other to a complex or salt of the complementary metal (i.e., cis,cis,trans-[RuCl3(CO)2(PTA-xP)] (5), trans-[RuCl3(PTA-xP)] (7), Zn(CH3COO)2, and ZnCl2). The molecular compounds 1, 3, trans-[[RuCl3(PTA-xP)](Zn(TPP))4] (8), and [([Ru(TPP)(PTA-xP)][PTA-xP,N])4{ZnCl2(OH2)}] (11) as well as the polymeric species [([Ru(TPP)(PTA-xP,N)]4{Zn(TPP)})∞ (4), cis,cis,trans-[[RuCl3(CO)2(PTA-xP)]4{Zn(TPP)}]∞ (6), trans-[[RuCl3(PTA-xP,N)]4{Zn(TPP)}]∞ (9), and [([Ru(TPP)(PTA-xP,N)]4{Zn10(CH3COO)16(CH3OH)2(OH2)]}∞ (10), were structurally characterized by single crystal X-ray diffraction. Compounds 4, 6, 9, and 11 are the first examples of solid-state porphyrin networks mediated by PTA. In 4, 6, 8, 9, and 11 the bridging PTA has the x3P,N binding mode, whereas in the 2D polymeric layers of 10 it has the triple-bridging mode x8P,2N. The large number of compounds with the six-coordinate Zn(TPP) (the three polymeric networks of 4, 6 and 9, out of five compounds) strongly suggests that the stereoelectronic features of PTA are particularly well-suited for this relatively rare type of coordination. Interestingly, the similar 1D polymeric chains 4 and 6 have different shapes (zigzag in 4 vs “Greek frame” in 6) because the {trans-Ru(PTA-xP,N)4} fragment bridges two Zn(TPP) units with anti geometry in 4 and with syn geometry in 6. Orthogonal “Greek frame” 1D chains make the polymeric network of 9. Having firmly established the binding preferences of PTA toward Ru(II) and Zn(II), we are confident that in the future a variety of Ru/Zn solid-state networks can be produced by changing the nature of the partners. In particular, there are several inert Ru(II) compounds that feature two or more P-bonded PTA ligands that might be exploited as connectors of well-defined geometry for the rational design of solid-state networks with Zn—porphyrins (or other Zn compounds).
heteropolytopic PN₁ ligand and might also potentially bridge two or more metal ions with different HSAB preferences (Chart 1).

The bridging κ₃P,N coordination mode of PTA was found to be rather common, even though its first example, the heterobimetallic coordination polymer \([\{\text{Ru} \text{Cp}(\text{dmso-κS})-(\text{PTA-κ²P,N})_2\}\{\text{AgCl}_3\}]_{\alpha}\) was described by Romerosa, Peruzzini and co-workers only in 2005. Subsequently, Romerosa and co-workers described a series of water-soluble polymeric networks with Ag(I), and Cu(I)10 featuring a Ru–CN–Ru–M backbone (M = Au, Ni, Cd, Co). They are formed by inert \([\{\text{RuCp}(\text{PTA})_2\}(\mu-\text{CN})\{\text{RuCp}(\text{PTA})_2\}]\) moieties connected at both ends through bridging PTA-κ₃P,N ligands to metal anions (i.e., [Au(CN)]⁻, [NiCl₃]⁻, [CdCl₃]⁻, [CoCl₃]⁻). In addition, besides two discrete molecular entities featuring a (Re(III)(PTA-κ²P,N)M(II)) moiety (M = Cu, Zn), many other examples of PTA-driven polymeric networks with Ag(I), and Cu(I) — often with different ancillary ligands — were reported, mainly by Kirillov, Pombeiro and co-workers. In these structures PTA assumes double (κ₃P,N), triple (κ³P,2N), and even quadruple (κ₄P,3N) bridging coordination modes. An example of homometallic mixed-valence Cu(I/II) polymeric network, in which PTA binds to Cu(I) with the soft P atom and to Cu(II) with the hard N atom was also described. Taken together, the results with Ag(I) and Cu(I) suggest that these metal ions are rather promiscuous toward PTA, without a marked preference for N- or P-bonding.

There are instead relatively few examples of complexes containing exclusively N-bonded PTA (PTA-κ₃N). They concern hard metal ions such as Mn(II) and Co(II), or the d¹⁰ metal ion Zn(II). After the first Zn–PTA complex — the distorted tetrahedral [ZnCl₂(PTA-κN)₂] — was described in 2009 by Pombeiro and co-workers,16,17 Reek, Kleij et al. investigated the reactivity of PTA with a number of square-planar Zn(salphen) complexes (salphen = N,N'-bis(salicylidene)imine-1,2-phenylenediamine) in the context of supramolecular catalysis. It was found that PTA binds to zinc exclusively through the N atoms and can act as a bridge between two or even three Zn(salphen) units, giving \([\{\text{Zn(salphen)}\}_2\text{(PTA-κ²N)}\] and \([\text{Zn(salphen)}\}_3\text{(PTA-κ³N)}\] adducts in which the zinc ions have a distorted square planar geometry.

In the past we and others have explored the coordination chemistry of PTA toward Ru compounds (where it binds through P exclusively).16,17 We have also largely exploited the axial coordination of Ru and Zn porphyrins toward polycyctenate pyridyl ligands for the construction of numerous supramolecular assemblies.18,19 Considering that, according to the literature, PTA binds always through P to ruthenium and through N to zinc, we reasoned that it might be exploited as an orthogonal bridging ligand for the preparation of heterobimetallic supramolecular assemblies and/or polymeric networks containing Ru– and Zn–porphyrins. In addition, the presence of PTA might improve their solubility in water or at least in protic solvents.

Phosphine ligands have high association constants with Ru–porphyrins, in the range of 10⁶ to 10⁸ M⁻¹, whereas N ligands, in particular hard tertiary amines, have lower constants. For example, it has been reported that Ph₂P-(CH₂)₂NEt₂ binds to ruthenium porphyrins exclusively through P and the NEt₂ group remains dangling. Zn–porphyrins make less robust axial bonds with N-ligands (compared to Ru), that depend also on N hybridization. For example, the association constant of pyridine with Zn(TPP) (TPP = meso-tetraphenylporphyrin) was found to be 7.7 × 10⁵ M⁻¹ (CH₂Cl₂, 25 °C), whereas under the same — or very similar — conditions amines (including tertiary amines) have ca. 10-fold larger association constants.22,23 By comparison, hexamethylenetetramine (HTMA) — the all-nitrogen analogue of PTA — was found to make stronger axial bonds with Zn–porphyrins compared to pyridyl functions (probably also because of its low steric demand), and binding constants in the range 10⁵ to 10⁶ M⁻¹ were measured for the axial N-binding of PTA to square planar Zn(salphen) complexes in toluene.15

The interactions of PTA with Ru– and Zn–porphyrins have not been investigated before. Thus, in this work we first established the coordination mode of this ligand toward the neutral model metallo-porphyrins [Ru(TPP)(CO)] and Zn(TPP), obtaining the mononeric adducts [Ru(TPP)(PTA-κ¹P,N)] (1) and [Zn(TPP)(PTA-κ¹N)] (3), in which PTA is axially bound to the metal inside the porphyrin. Then, we prepared and structurally characterized a number of heterobimetallic Ra/Zn porphyrin polymeric networks mediated by P,N-bridging PTA (PTA-κ²P,N) and, in one case, (PTA-κ³P,2N). In such assemblies either both metal centers reside inside a porphyrin core or one of the two belongs to a coordination compound. Our findings demonstrate that indeed PTA behaves as a selective orthogonal ligand, binding to Ru exclusively through the P atom and to Zn exclusively through the N atoms.

Figure 1. ¹H NMR spectra (CDCl₃) of PTA (top) and [Ru(TPP)(PTA-κ¹P)] (1) (bottom).
RESULTS AND DISCUSSION

Reactivity of [Ru(TPP)(CO)] toward PTA. It is well-known from the literature that whereas pyridine or azole ligands (N) replace the labile solvent molecule trans to CO in [Ru(por)(CO)(S)] compounds (e.g., por = TPP; S = MeOH or EtOH, typically not indicated in the formula), affording derivatives of the general formula [Ru(por)(CO)(N)],25–28 most phosphine and phosphite ligands (P) under mild conditions replace easily also the carbonyl ligand yielding disubstituted compounds of formula [Ru(por)(P)2].20,29–35 Monosubstituted [Ru(por)(CO)(P)] intermediates with tertiary phosphines have been occasionally isolated,31 whereas in most other cases, due to the weakening of the carbonyl ligand by the phosphine trans effect, they could not be isolated but were characterized spectroscopically in solution.20a To our knowledge, with the exception of a private communication from Sanders and co-workers,36 no X-ray structure of such an intermediate has been reported yet.

We found that PTA reacts with [Ru(TPP)(CO)] as do most other phosphines. When treated with a slight excess of PTA in chloroform solution at room temperature, [Ru(TPP)(CO)] rapidly affords [Ru(TPP)(PTA-xP)2] (1) in high yield. Axial coordination of two trans PTA moieties, bound through the P atom, was clearly evident from NMR spectroscopy (Figure 1). The 31P resonance, which is not significantly affected by the porphyrin shielding cone, occurs as a singlet at −50.6 ppm, i.e., in the typical region for mutually trans PTA adducts to Ru(II).16c The 1H resonances of the PTA methylene protons, and those of the PCH2N protons in particular, are shifted to lower frequencies compared to free PTA because the protons fall in the shielding cone of the porphyrin. Thus, the NCH2N protons, closer to the macrocycle, give a singlet (12H) at −0.26 ppm. The assignments were confirmed by the HSQC spectrum (Figure S3), since the corresponding carbon atoms have characteristic and well-resolved resonances that are only marginally affected by coordination.1 The βH singlet of TPP is shifted to lower frequencies by ca. 0.35 ppm by the replacement of CO with two PTAs. Even though the chemical shifts of the phenyl signals are not particularly affected, by virtue of the increased shielding symmetry the oH resonance—that was split into two well-resolved doublets in the spectrum of [Ru(TPP)(CO)]—is a sharp doublet in that of [Ru(TPP)(PTA-xP)2] (Figure 1 and Figure S1). Consistent with what found with similar [Ru(por)(P)2] adducts,20,29–35 the Soret band in the electronic absorption spectrum of 1 is considerably red-shifted compared to [Ru(TPP)(CO)] (431 vs 408 nm).

The geometry of 1 was confirmed by single crystal X-ray analysis (Figure 2). The Ru–P distance in 1 compares well with those in similar [Ru(por)(P)2] compounds as well as with those in Ru(II) coordination compounds that feature the {trans-Ru(PATA-xP)2} fragment (Table 1).16,20,31

Finally, compound 1 was rapidly obtained at room temperature also upon addition of two equiv of PTA to a CDCl3 solution of [Ru(TPP)(CO)(py)] (py = pyridine), thus demonstrating that, besides ethanol, PTA also readily replaces axially bound pyridine.

Regrettfully, compound 1 was found to be completely insoluble in water, even at acidic pH where protonation of PTA would be expected to improve solubility. For instance, the
multiple equilibria can occur as in the case of Zn(salphen)–(PTA-κN) adducts, where PTA can bind axially up to three Zn(salphen) units. In addition, even though zinc porphyrins are expected to bind preferentially one axial N ligand making square pyramidal adducts, the formation of octahedral products with two axial ligands is not uncommon and cannot be excluded.

Thus, the NMR spectrum is expected to depend also on the concentration and temperature, in addition to the PTA/Zn ratio. To be noted that, consistent with N-coordination of PTA to Zn(TPP) (and contrary to what observed for 1, in the 1H NMR spectrum at high Zn(TPP)/PTA ratio the resonance of the NCH2N protons is shifted more upfield than the NCH3P resonance (Figures S6 and S7).

Slow diffusion of diethyl ether onto the chloroform solution of the PTA/Zn(TPP) = 0.5 mixture afforded crystals of the discrete [Zn(TPP)(PTA-κN)] adduct (3), whose X-ray structure is shown in Figure 3. As clear also from the lattice representation (Figure S13), zinc is five-coordinate (i.e., binds to a single PTA molecule), and each PTA is bound to a single Zn(TPP) unit.

![Figure 3. ORTEP representation (50% probability ellipsoids) of the crystal structure of complex [Zn(TPP)(PTA-κN)]·H2O·CHCl3 (3·H2O·CHCl3). For the sake of clarity, H atoms, one disordered water, and one CHCl3 crystallization molecule are omitted. The Ph1–Ph4 labels allow one to visualize on the figure the dihedral angles reported in Table S3.](https://dx.doi.org/10.1021/acs.inorgchem.0c00080)

| compound                | Ru–P distance (Å) | ref     |
|-------------------------|-------------------|---------|
| [Ru(TPP)(PTA-κP)2]14    | 2.353(7)          | this work |
| [Ru(TPP)(dpm)2]        | 2.398(3)          | 31a     |
| [Ru(OEP)(PPh3)2]15     | 2.428 (average)   | 31c     |
| [Ru(OEP)(dpap)2]15     | 2.3777(5)         | 20c     |
| [Ru(DPP)(dpap)2]15     | 2.340(5)–2.3623(10) | 20a    |
| [Ru(TPP)(dpap)2]46     | 2.3597(10)–2.3784(10) | 20c    |
| Ru(II) compounds with {trans-Ru(PTA-κP)2} fragment | 2.290–2.400 | 16c |

As already observed for N-coordination of PTA, as well as for protonation and alkylation, the N21–C bond distances are slightly elongated—compared to the other N–C distances—upon coordination to Zn. The axial Zn–N(PTA) bond length is longer than in the distorted tetrahedral complex [ZnCl2(PTA-κN)2]14 (and in similar complexes with O==PTA and S==PTA), but compares rather well with those found in the square-pyramidal Zn(salphen)–(PTA-κN) adducts where PTA occupies the axial position (Table 2). 15

**PTA-Bridged Heterobimetalllic Ru/Zn Compounds.**

The above results indicate that the axial binding of PTA toward Ru– and Zn–porphyrins is truly orthogonal and might be exploited to create heterodinuclear supramolecular porphyrin assemblies connected by bridging PTA moieties.

Thus, we investigated the interaction between [Ru(TPP)-(PTA-κP)2]14 (1) and Zn(TPP). An NMR titration of Zn(TPP) into a CDCl3 solution of 1, in which the Zn(TPP)/I ratio ranged from 1 to 4 (Figure S8) showed that the PTA resonances were broadened and gradually shifted to lower frequencies upon increasing the number of Zn(TPP) equivalents. Conversely, the resonances of the two porphyrins, as well as the 31P{1H} resonance of PTA, were only marginally affected. These findings are consistent with the establishment of an axial Zn–(PTA-κN) labile interaction between the stable and inert Ru–(PTA-κP) moieties and Zn(TPP). In further agreement with this hypothesis the final spectrum of this series was substantially coincident with that obtained by adding 2 equiv of PTA to a 1:4 mixture of [Ru(TPP)(CO)] and Zn(TPP) (Figures S9 and S10), indicating that PTA discriminates between Ru and Zn even when it is not preventively bound to Ru and is in the presence of a stoichiometric excess of Zn.

**Table 1. Ru–(PTAκP) Bond Lengths in the X-ray Structurally Characterized Compounds**

| compound                | Ru–P distance (Å) | ref     |
|-------------------------|-------------------|---------|
| [Zn(TPP)(PTA-κN)] (3)   | 2.186(2)          | this work |
| [ZnCl2(PTA-κN)]2       | 2.053(3)–2.101(3) | 14      |
| [ZnCl2(O = PTA-κN)(OH2)] | 2.0931(10) | 46      |
| [[Zn(salphen)]2(PTA-κN)] | 2.103(6), 2.172(7) | 15    |
| [[Zn(salphen)]2(PTA-κN)] | 2.194(4), 2.201(4), 2.200(3) | 15 |
| [Zn(TOHPP)(HTMA)] (TOHPP = tetra(4-hydroxyphenyl)porphyrin) | 2.520(2) | 24 |
| [Zn(TCPP)(HTMA)] (TCPP = tetra(4-carboxyphenyl)porphyrin) | 2.510(2) | 24 |
| [Zn(TPyP)(HTMA)] (TPyP = tetra(4′-pyridyl)porphyrin) | 2.189(3) | 24 |

**Table 2. Zn–(PTAκN) and Zn–(HTMA-κN) Bond Lengths in the X-ray Structurally Characterized Compounds**

| compound                | axial Zn–N distance (Å) | ref     |
|-------------------------|-------------------------|---------|
| [Zn(TPP)(PTA-κN)] (3)   | 2.186(2)          | this work |
| [ZnCl2(PTA-κN)]2       | 2.053(3)–2.101(3) | 14      |
| [ZnCl2(O = PTA-κN)(OH2)] | 2.0931(10) | 46      |
| [[Zn(salphen)]2(PTA-κN)] | 2.103(6), 2.172(7) | 15    |
| [[Zn(salphen)]2(PTA-κN)] | 2.194(4), 2.201(4), 2.200(3) | 15 |
| [Zn(TOHPP)(HTMA)] (TOHPP = tetra(4-hydroxyphenyl)porphyrin) | 2.520(2) | 24 |
| [Zn(TCPP)(HTMA)] (TCPP = tetra(4-carboxyphenyl)porphyrin) | 2.510(2) | 24 |
| [Zn(TPyP)(HTMA)] (TPyP = tetra(4′-pyridyl)porphyrin) | 2.189(3) | 24 |
Adjacent Ru/Zn units are connected by a PTA bridging ligand which coordinates to Ru through the phosphorus atom and to Zn through one of the nitrogen atoms (Figures S14–S16). Thus, both Ru and Zn are six-coordinate and feature two equal axial ligands. Each \(\text{\{trans-Ru(PTA)\}}\) unit binds two zinc atoms with anti geometry, thus generating the zigzag motif. Since the equatorial environment of Ru and Zn is identical and the P/N bonding modes of the PTA ligand are nearly geometrically equivalent, the symmetry of the observed diffraction pattern (space group \(\text{C}2/c\)) does not distinguish the two metal ions and the corresponding PTA binding modes. This leads to a crystallographically independent fragment in which a single metal site (M) is equally partitioned between Ru and Zn and, correspondingly, two symmetry related binding sites (L) of the PTA are partitioned at 50% between Ru and Zn and, correspondingly, two symmetry related the two metal ions and the corresponding PTA binding modes. The equatorial environment of Ru and Zn is identical and the P/N bonding modes of the PTA ligand are nearly geometrically equivalent, the symmetry of the observed diffraction pattern (space group \(\text{C}2/c\)) does not distinguish the two metal ions and the corresponding PTA binding modes. This leads to a crystallographically independent fragment in which a single metal site (M) is equally partitioned between Ru and Zn and, correspondingly, two symmetry related binding sites (L) of the PTA are partitioned at 50% between Ru and Zn.

Only half of the Ru and Zn units are crystallographically independent. In the Ru complex, the trans C2 carboxyl and C12 ligands exchange their positions around a 2-fold axis due to disorder: only one of the two identical populations is represented. Labels Ph1 and Ph2 allow one to visualize on the figure the dihedral angles reported in Table S4.

Figure 4. ORTEP representation (50% probability ellipsoids) of the “monomeric” unit of the polymeric zigzag chains which constitute the crystal structure of compound \([\{\text{Ru(TPP)(PTA-kP,N)}\}_2\{\text{Zn(TPP)}\}]\) (4) (hydrogen atoms and minor population of one disordered phenyl group omitted for clarity). Labels Ph1 and Ph2 allow one to visualize on the figure the dihedral angles reported in Table S4.

NMR titration of Zn(TPP) (from 2 to 4 equiv) into a CDCl\(_3\) solution of \(\text{5}\) were similar to those described above with \(\text{1}\), i.e., upfield shift and broadening of the PTA proton resonances (Figure S11). Also in this case, the \(31^\text{P}\) resonance was not particularly affected by the addition of Zn(TPP) and occurred as a singlet at \(-48.9\) ppm (to be compared with \(-51.0\) ppm in the free complex), indicating that the Ru complex remains intact.

X-ray quality single crystals of the 1D polymeric compound cis,cis,trans-\([\{\text{RuCl}_2(\text{CO})_2(\text{PTA-kP,N})\}_2\{\text{Zn(TPP)}\}]\)\(_\infty\) (6) were obtained upon diffusion of diethyl ether onto a chloroform solution of a 2:1 mixture of Zn(TPP) and 5. The crystal structure of compound 6 (Figure 5) is similar to that of 4 and consists of parallel polymeric chains in which the Zn atom of each Zn(TPP) is six-coordinate and binds axially two PTA ligands belonging to different Ru complexes. However, since each Ru complex bridges two Zn(TPP) units with \(\text{syn}\) geometry, the resulting chain has “Greek frame” shape (rather than zigzag as in 4) (Figure S17). The two polymeric chains of 4 and 6 are compared in Figure 6.

Conversely, the crystallization of Zn(TPP) with another symmetrical Ru–P TA complex, \(\text{trans-}\{\text{RuCl}_2(\text{PTA-kP})\}_2\) (7),16,17 afforded different results, depending on the Zn/P TA ratio adopted. Using a stoichiometric or a slight excess of Zn(TPP) (i.e., Zn/P TA = 1 or 1.5) the discrete molecular species \(\text{trans-}\{\{\text{RuCl}_2(\text{PTA-kP,N})\}_2\{\text{Zn(TPP)}\}]\)\(_\infty\) (8, Figure 7 and Figures S19–S21), in which each one of the four coplanar PTA ligands of 7 is axially bound through an N atom to a five-coordinate Zn(TPP), was obtained.

The four porphyrins in 8 lay alternatively above and below the equatorial plane of the Ru complex, generating a very compact arrangement (Figure S21) that closely resembles that of the porphyrin pentamer \([\text{Zn(3TPyP)}]\{\text{Ru(TPP)(CO)}\}_5\) (3TPyP = \(5\)-tetra(3′-pyridyl)porphyrin) described by us 20 years ago.49 Similarly to what found for 6, when
redissolved in CDCl₃ the crystals of 8 give a singlet in the ³¹P{¹H} NMR spectrum at −51.1 ppm (cfr −50.6 ppm in 7). Conversely, when a defect of Zn(TPP) was used (Zn/PtP = 0.5) crystals of the polymeric network trans-[[RuCl₂(µ-PTA-k²P,N)₄]₂[Zn(TPP)]₄]∞ (9) were obtained. In 9, each Ru center is surrounded by four Zn (TPP) units with a geometry very similar to that found in 8. However, in this case the Zn atoms are six-coordinate, thus originating a 3D polymeric network (Figure 8), with a texture of orthogonal 1D threads that intersect each other at every Ru center (Figure 9). Each 1D thread of the network, originated by a \{trans-Ru(PTA-k²P,N)₃\} fragment, has the “Greek frame” shape found in 6.

Consistent with what observed above (Table 2), the axial Zn–N bond length in six-coordinate 9 (2.4869(2) Å) is similar to that found in 6 (2.534(2) Å), and remarkably longer than that in five-coordinate 8 (2.242(6) Å).

The crystallization of [Ru(TPP)](PTA-kP)₂ (1) with a ca. 8:1 excess of Zn(CH₃COO)₂ afforded crystals of [[Ru(TPP)-(PTA-kP,2N)]₂]{Zn₉(CH₃COO)₁₆(CH₂OH)₂(OH)₂}·3CHCl₃ (10·3CHCl₃). The crystal structure of compound 10 (Figure 10) can be described as a stack of 2D polymeric layers, almost perfectly parallel to the plane defined by the b axis and the diagonal of the ac face of the unit cell. Each polymeric layer contains the Ru porphyrin and an intricate neutral Zn–acetate cluster in 1:1 ratio (for the description of the Zn₉ cluster see the Supporting Information). The Ru and the central Zn atom (Zn4) sit on inversion points, so that only half of the Ru porphyrin and Zn cluster are crystallographically independent. Four Zn atoms of each cluster are N-bound to four PTA ligands of different Ru(TPP) units, and correspondingly, each Ru porphyrin connects with four Zn clusters, two for each axial PTA ligand (Figure 11). Thus, in this case PTA has a triple-bridging k²P,N binding mode.

Due to the layered structure, the unit cell contains a cavity whose volume amounts to 16% of the total (see Experimental Section).

By changing the nature of the zinc salt a remarkably different compound was obtained. In fact, diffusion of n-hexane into a chloroform/ethanol solution of a 1:2 mixture of 1 with ZnCl₂ afforded crystals of the dinuclear compound [[Ru(TPP)-(PTA-kP)]₂[ZnCl₂(OH₂)] (11) in which one of the two trans PTA-kP ligands of 1 binds through an N atom to a ZnCl₂(OH₂) fragment (Figure 12). The distorted tetrahedral coordination environment of the Zn atom is similar to that found in [ZnCl₂(OH₂)(PTA=O)]. The crystal structure consists of an arrangement of parallel 1D sequences of molecules of complex 11, oriented along the [101] direction, with a shape that closely resembles the “Greek frame” found in 6 and 9 (Figure S25). Regrettably, due to the low quality of the X-ray data (see also the Experimental Section for details) the expected slight elongation of the PTA C–N11(Zn) bond distances could not be detected.

### CONCLUSIONS

In this work, we demonstrated that PTA (1,3,5-triaza-7-phosphaadamantane) behaves as an orthogonal ligand between Ru(II) and Zn(II), since it selectively binds through the P atom to ruthenium and through one or more of the N atoms to zinc. This property of PTA was first exploited by us for preparing the two monomeric porphyrin adducts [Ru(TPP)-(PTA-kP)]₂ (1) and [Zn(TPP)-(PTA-kP)] (3), in which PTA is axially bound to the inner metal. Then, we prepared a number of heterobimetallic Ru/Zn porphyrin polymeric networks—and two discrete species—mediated by P₉N-bridging PTA in which either both metals reside inside a porphyrin core, or one metal belongs to a porphyrin, either Ru(TPP) or Zn(TPP), and the other to a complex or salt of the complementary metal (i.e., cis,cis,trans-[RuCl₂(CO)₂(PTA-kP)]₂ (5), trans-[RuCl₂(PTA-kP)] (7), Zn(CH₃COO)₂, and ZnCl₂). Both the molecular compounds 1, 3, trans-[RuCl₂(PTA-kP,2N)]₄[Zn(TPP)]₄ (8), and [[Ru(TPP)-(PTA-kP)]₂(ZnCl₂(OH₂))] (11), and the polymeric species [[{Ru(TPP)(PTA-k²P,N)₃}[Zn(TPP)]₄]∞ (4),
cis,cis,trans-[RuCl₂(PTA-κ₂P,N)₂[Zn(TPP)]₃]∞ (9), trans-[RuCl₂(PTA-κ₂P,N)₄[Zn(TPP)]₀ (9), and [Ru(TPP)(PTA-κ₂P,N)₂{Zn₉(CH₃COO)₁₆(CH₃OH)₂(OH)₂}·3CHCl₃]∞ (10) have been structurally characterized by single crystal X-ray diffraction. The number of compounds with the relatively rare six-coordinate Zn(TPP) (three, the polymeric networks of 4, 6, and 9, out of five) is largely above-average (see ref 45), strongly suggesting that the stereoelectronic features of PTA are particularly well-suited for this type of coordination. In 4, 6, 8, 9, and 11 the bridging PTA has the κ₂P,N binding mode, whereas in the 2D polymeric layers of 10 it has the triple-bridging mode κ₃P₂N. In one case, we demonstrated that, by tuning the PTA/Zn(TPP) ratio, it is possible to control the number of axial Zn–N coordination bonds and thus to switch from a molecular species (8, five-coordinate Zn) to a 2D polymeric network (9, six-coordinate Zn). Similarly, we are confident that also in the case of 11 by operating at higher Ru/ZnCl₂ ratios a second PTA ligand (from a different 1) is likely to replace the residual water molecule on the Zn fragment, thus affording a polymeric network upon crystallization. Interestingly, we also found that when Zn(TPP) is sandwiched between two (trans-Ru(PTA-κ₂P,N)₃ fragments, similar 1D polymeric chains with two different shapes—zigzag in 4 vs “Greek frame” in 6 and 9—are obtained depending on whether the connecting bonds of each Ru fragment have an anti (4) or syn geometry (6 and 9).

Due to the rather weak and labile nature of the Zn–N(PTA) bond, and consistent with literature data about Zn–PTA...
The compounds are not stable in solution and disassemble into the mononuclear fragments in concentration-dependent equilibria. Thus, their main interest resides in solid states. The two N–Zn bonds connecting the second (lower) PTA ligand to corresponding Zn clusters are also shown, together with the four connections of each Zn cluster with the N atoms of PTA ligands belonging to four distinct [[Ru(TPP)(PTA-xPzNz)]2] units. Labels Ph1 and Ph2 allow one to visualize on the figure the dihedral angles reported in Table S8. Color code: Ru (light purple), Zn (green), P (yellow), N (blue), O (red).

**EXPERIMENTAL SECTION**

**Materials.** All chemicals, including TLC silica gel plates, were purchased from Sigma-Aldrich and used as received. Solvents were of reagent grade. The ruthenium precursor cis,cis,trans-[RuCl2(CO)2(PTA-xPzNz)]] (5), trans-[RuCl2(PTA-xPzNz)] (7), and the porphyrins TPP, Zn(TPP) were synthesized and purified as previously reported by us or by others.

**Instrumental Methods.** Mono- and bidimensional (1H-1H COSY, 1H-13C HSQC) NMR spectra were recorded on a Varian 400 or 500 spectrometer (1H: 400 or 500 MHz, 13C [1H]: 161 or 202 MHz). 1H chemical shifts were referenced to internal 85% H3PO4 at 0.00 ppm. ESI mass spectra were collected in the positive and the uncoordinated N atoms of PTA in the networks might undergo protonation, thus introducing positive charges and the possibility of making additional electrostatic and H-bonding interactions.

We believe that the examples reported in this work represent robust proofs-of-concept that firmly establish the binding preferences of PTA toward Ru(II) and Zn(II), and are confident that a variety of discrete species and networks can be produced by changing the nature of the Ru and Zn partners and their ratio. In particular, there are several inert Ru(II) compounds (in addition to 5 and 7) that feature two or more P-bonded PTA ligands that might be exploited as linkers of well-defined geometry for the rational design of solid state networks with Zn–porphyrins (or other Zn compounds). The remaining ancillary ligands on the Ru center would allow to fine-tune the properties of the network, e.g., by providing interactions for the selective binding of host molecules. Finally, the uncoordinated N atoms of PTA in the networks might underlie protonation, thus introducing positive charges and the possibility of making additional electrostatic and H-bonding interactions.
defined and streaky spots were apparent. A translocation vector \((0,1/2,0)\) could be found by assuming that the intense peak near the Ru site was due to another Ru atom of the translocated lattice and by matching the distance of the LTED peak from the Ru site (at \((1/2,0.79,1/2)\)). The measured reflection intensities were then corrected according to eq 3 in ref 60. An optimal value of 0.094 for the translocated cell fraction could be found by trial and error until the intensities of the two peaks due to the LTED were reduced to negligible values.

For compound 9, no Fourier peaks of appreciable intensity could be located inside the mentioned cavity, which was then assumed to contain heavily disordered methanol solvent molecules and modeled with the Squeeze procedure of the PLATON code.61 The “squeezed” electronic charge was 148 (in electron charge units), corresponding to about eight methanol solvent molecules.

In the asymmetric unit of the crystal structure of complex 11, the \([\text{ZnCl}_2(\text{OH}_2)]\) group is very close to a 2-fold axis, thus ruling out the possibility that it is present on both PTX ligands of the same Ru complex: in this case, two \([\text{ZnCl}_2(\text{OH}_2)]\) groups of adjacent Ru complexes would overlap (Figure S25). For this reason, we refined a model in which the \([\text{ZnCl}_2(\text{OH}_2)]\) has a total occupation factor of 0.5, which ensures a Ru:Zn ratio of 1:1 (also the Ru atom sits on a special position with occupation factor 0.5). An additional complication is that the \([\text{ZnCl}_2(\text{OH}_2)]\) group is disordered over two positions, which led to a further partition of the 0.5 occupation factor into two populations with occupations of 0.3 and 0.2, respectively (Figure S26).

**Synthesis of the Complexes.** \([\text{Ru}^{\text{II}}(\text{TPP})(\text{PTA}-\text{P})]_{n/2} \cdot \text{CHCl}_3\) (1). A 20 mg amount of \([\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})] \cdot \text{CDCl}_3\) (0.027 mmol) was dissolved in 8 mL of chloroform, obtaining X-ray quality single crystals by slow diffusion of diethyl ether into chloroform solution of a 1:2 mixture of \([\text{Ru}^{\text{II}}(\text{TPP})(\text{PTA}-\text{P})]_{n/2} \cdot \text{CHCl}_3\) (5, 6.1 mg, 0.011 mmol) and \([\text{Zn}^{\text{II}}] \cdot \text{CDCl}_3\) (2.5 mg, 2 equiv). \(^{31}\text{P}^1\text{H} \) NMR (CDCl\(_3\)) \(\delta \) (ppm): -49.0 (s).

\(\text{trans}-[(\text{Ru}^{\text{II}}\text{Cl}_2(\text{PTA}-\text{P})\text{Zn}^{\text{II}}\text{N})_2]\text{CHCl}_3 \cdot 0.6\text{CHCl}_3\) (9,4-CHCl\(_3\)). X-ray quality crystals of 9,4-CHCl\(_3\) were obtained upon diffusion of hexane into 4 mL of a 1:2 chloroform solution of \(\text{trans}-[(\text{Ru}^{\text{II}}\text{Cl}_2(\text{PTA}-\text{P})\text{Zn}^{\text{II}}\text{N})_2]\text{CHCl}_3 \cdot 0.6\text{CHCl}_3\) (11, 0.6CHCl\(_3\)). X-ray quality crystals of 11,0.6CHCl\(_3\) were obtained by slow diffusion of n-hexane onto 2.4 mL of a 1:2 chloroform/ethanol solution of a 1:2 mixture of \([\text{Ru}^{\text{II}}(\text{TPP})(\text{PTA}-\text{P})]_{n/2}\) (1, 3 mg, 0.0023 mmol) and \([\text{Zn}^{\text{II}}] \cdot \text{CDCl}_3\).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00080.

Details of X-ray data collection and refinement for compounds 1, 3, 4, 6, 8–11, mono- and bidimensional NMR spectra of the reported compounds, additional drawings for the X-ray structures, a description of the Zn–acetate cluster of compound 10, and additional comments on the X-ray structure of compound 11 (PDF)

**Accession Codes**

CCDC 1964277, 1964280–1964285, and 1964342 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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Due to the low quality of the X-ray data, the observed electron density map of the disordered \([\text{ZnCl}_2(\text{OH}_2)]\) fragment could be modeled also by a ZnCl\(_2\) fragment. Protonation of the opposite PTA ligand \(\text{PTAH}^+\) would balance the negative charge, yielding the zwitterionic molecule \([\text{Ru}(\text{TPP})(\text{PTAH}^+)(\text{PTA}^2\text{P})]\) (see Supporting Information for further details).

The pioneering work of Israel Goldberg in studying microporous structures based on porphyrin building units cannot be easily cited, due to its vastness. It can perhaps be best appreciated by reading this commemorative article, and the references cited therein: Titi, H. M.; Konar, S. The Voyage of Goldberg: Supramolecular Chemistry and Memories. Cryst. Growth Des. 2019, 19, 3603–3606.

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