DOI: 10.1002/ejic.200601152

The First Copper Complexes Bearing the 1,3,5-Triaza-7-phosphaadamantane (PTA) Ligand

Alexander M. Kirillov,[a] Piotr Smoleński,[a] M. Fátima C. Guedes da Silva,[a] and Armando J. L. Pombeiro*[a]

Keywords: Copper / N,P ligands / Structure elucidation / Phosphane ligands

The Cu^I compound $[Cu(PTAH)_4](NO_3)_5$ (**1**) {PTAH = *N*-protonated form of 1,3,5-triaza-7-phosphaadamantane (PTA)} was easily prepared by reacting hydrated $Cu(NO_3)_2$ and PTA in aqueous acidic solution at room temperature. Further treatment of **1** with sodium hydroxide in water led to an unprotonated PTA derivative $[Cu(PTA)_4](NO_3)$ (**2**). Both compounds are water-soluble and air-stable, and were characterized by IR, ^1H-, $^{13}C\{^1H\}$-, $^{31}P\{^1H\}$- and ^{63}Cu NMR spectroscopy, FAB-MS(+), elemental and single-crystal X-ray diffraction structural analyses. They exhibit a nearly regular tetrahedral coordination environment about each copper centre filled by the phosphorus atoms of the four PTAH/PTA moieties, which show distinct and unusual geometrical arrangements if viewed along the P–Cu bonds. The $^{31}P\{^1H\}$- and ^{63}Cu NMR spectra of **2** in D_2O solution show spin coupling between the ^{31}P and ^{63}Cu nuclei at room temperature. These compounds represent the first examples of Cu complexes bearing PTA or any derived ligand with a cagelike PTA core and expand the restricted family of aqua-soluble copper phosphane complexes.

Introduction

The coordination chemistry of the aqua-soluble phosphane 1,3,5-triaza-7-phosphaadamantane (PTA) and derived species has received increased attention in recent years.[1] This is mainly due to the good solubility of transition-metal PTA complexes in water, thus making possible their efficient application in aqueous phase catalysis,[2] as water-soluble antitumor agents[1,3] and as photoluminescent materials.[1,4] In particular, one of us has reported that Rh and Ru complexes with PTA or its *N*-alkylated derivatives are catalysts for the hydrogenation, hydroformylation and isomerization of alkenes.[5]

However, although a large variety of copper phosphane complexes has been reported,[6] known water-soluble examples remain rather scarce and include compounds with, for example, tris(*m*-sulfonatophenyl)phosphane,[7a] tris(hydroxymethyl)phosphane,[7b] tris(*m*-tolyl)phosphane[7c] and tris(*p*-fluorophenyl)phosphane[7c] [the aqua solubility of the last two examples should arise from the other ligands such as dihydrobis(3-nitro-1,2,4-triazol-1-yl)borate]. Moreover, the Cu–PTA chemistry is virtually unknown;[1] only one study reported the formation of $[Cu_nS_m(PTA)]^-$ (n = 1, 2, 4 and 5; m = 2–4) species in the gas phase under the Fourier transform ion cyclotron resonance (FTICR) mass spectrometry conditions,[8] whereas there are no examples of *isolated* copper complexes with PTA or its derivatives. In contrast, more than 100 complexes with a cagelike PTA core and with other transition metals have already been synthesized[1,3–5,9] and structurally characterized.[6]

By extending PTA coordination chemistry to our recent studies on the synthesis of water-soluble Cu complexes with other ligands (which catalyze the mild functionalization of alkanes),[10] we now report the easy synthesis of the new aqua-soluble Cu^I–PTA compounds $[Cu(PTAH)_4](NO_3)_5$ (**1**) and $[Cu(PTA)_4](NO_3)$ (**2**). They constitute, as far as we are aware of, the first isolated examples of copper complexes bearing PTA or any derived ligand with a cagelike PTA core. They were characterized by IR, ^1H-, $^{13}C\{^1H\}$-, $^{31}P\{^1H\}$- and ^{63}Cu NMR spectroscopy, FAB-MS(+), elemental and single-crystal X-ray diffraction structural analyses.

Results and Discussion

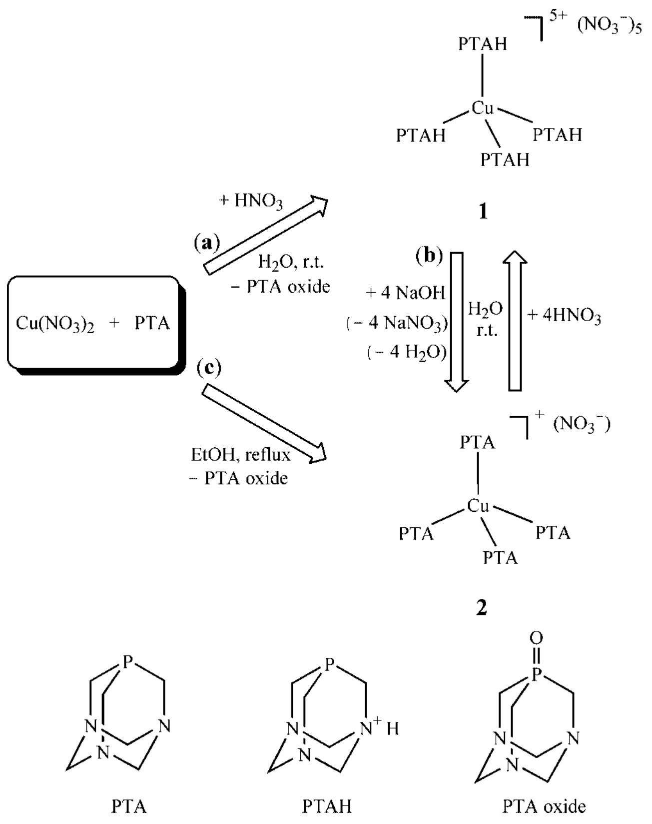
Synthesis and Spectroscopic Characterization

Addition of an excess of PTA to an acidic aqueous solution of Cu^{II} nitrate provided the formation, at room temperature and in air, of the cationic Cu^I complex $[Cu(PTAH)_4](NO_3)_5$ (**1**) by a redox process resulting in the reduction of Cu^{II} to Cu^I and partial oxidation of PTA to the corresponding phosphane oxide (Scheme 1, **a**), which was identified by $^{31}P\{^1H\}$ NMR spectroscopic data of the reaction mixture and by the unit-cell parameters of isolated single crystals measured by X-ray diffraction which are in

---

[a] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,
Av. Rovisco Pais, 1049-001 Lisbon, Portugal
Fax: +351-21-846-4455
E-mail: pombeiro@ist.utl.pt

agreement with those already reported.[11] This correlates with the previously described[12] ability of PTA to act as a reductant and to stabilize low-oxidation metal states, thus leading to the synthesis of, for example, Pt^0, Pd^0, Ni^0 and Ru^{II} PTA complexes starting from the corresponding metal(II/III) chlorides.[5a,12] Compound **1** was further precipitated by addition of EtOH to the reaction mixture, and it was isolated as a white microcrystalline solid in 92% yield, based on Cu^{II} nitrate. Further treatment of **1** with 4 equiv. sodium hydroxide in water at room temperature (Scheme 1, **b**) led to the formation of the unprotonated derivative $[Cu(PTA)_4](NO_3)$ (**2**), which was isolated, upon recrystallization from MeOH, in 57% yield as a white microcrystalline solid. Compound **2** was also obtained directly (83% yield) from Cu^{II} nitrate upon reaction with an excess of PTA in refluxing EtOH (Scheme 1, **c**). Moreover, protonation of **2** led to **1**, thus showing the reversibility of their interconversion. Both compounds **1** and **2** are air-stable solids, which are soluble and stable in water ($S_{25\,°C} \approx 6$ and 64 $mg\,mL^{-1}$, respectively) and in DMSO solutions.



Scheme 1.

The IR spectra of **1** and **2** (KBr pellet) show a set of vibrations typical of coordinated PTAH/PTA, as well as broad and strong bands (1382 and 1363 cm^{-1}, respectively) due to the nitrate ions. The complex molecular ion with four unprotonated PTA ligands, $[Cu(PTA)_4]^+$, is clearly observed at $m/z = 691$ with the expected isotopic pattern in the FAB-MS(+) spectra of both compounds **1** and **2**, whereas the heaviest detected fragment ($m/z = 816$) $[Cu(PTA)_4 + 2Cu - 3H]^+$ results from coupling of the molecular ion with two copper ions. Other typical peaks correspond to the stepwise fragmentations by loss of one to four PTA ligands, followed in **1** by the recombination of obtained species with Cu^+.

The ^1H NMR spectra of both compounds, recorded in D_2O solution, show two types of methylene protons. Hence, the PCH_2N protons occur as a doublet at δ = 4.2 ppm ($^2J_{P-H}$ = 4.8 Hz) and as a broad singlet at δ = 4.1 ppm in **1** and **2**, respectively, while the AB spin system due to the $NCH_{ax}N$ and $NCH_{eq}N$ protons[13] is centred at $\delta \approx 4.8$ ppm ($^2J_{AB}$ = 7.0 Hz) (for **1**) and 4.6 ppm ($^2J_{AB}$ = 13.5 Hz) (for **2**). Their $^{13}C\{^1H\}$ NMR spectra are similar, presenting two broad singlets at δ ca. 74 and 53 ppm, assigned to the NCH_2N and PCH_2N carbon nuclei, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **1**, in D_2O, exhibits a broad singlet at δ = –82.5 ppm (Figure 1, **a**) which, on addition of an excess of free PTA or PTAH, shifts upfield (see parts **a** and **c**, respectively, in Figure 1) without observing a distinct resonance of the free phosphane ligand, which is consistent with fast exchange of coordinated and free phosphane ligands.

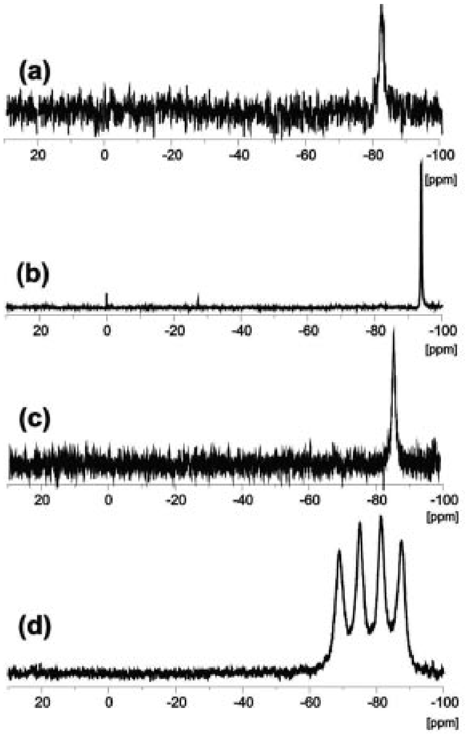


Figure 1. $^{31}P\{^1H\}$ NMR spectra of **1** in D_2O solution: (a) standard spectrum; (b, c) with an excess of added PTA (b) or PTAH (c); (d) at pH = 8.0 (after addition of NaOH, with formation of **2**).

The $^{31}P\{^1H\}$ NMR spectrum of **2** displays a 1:1:1:1 quartet at δ = –78.2 ppm ($^1J_{P-Cu}$ = 761 Hz) (Figure 1, **d**) which, in contrast to **1**, does not show appreciable change upon addition of an excess of free PTA; the spectrum is maintained with the appearance of the singlet of free PTA at δ = –95.0 ppm. This indicates that the mentioned fast phosphane exchange is not detected in the case of **2**, and the ^{31}P–^{63}Cu spin coupling (^{63}Cu and ^{65}Cu, $I = 3/2$) is observed. In agreement, the ^{63}Cu NMR spectrum of **2** (Figure 2) shows a 1:4:6:4:1 quintet, with the same $^{1}J_{P-Cu}$ at $\delta = 181.5$ ppm (relative to $[Cu(MeCN)_4][PF_6]$), although no ^{63}Cu resonance was detected in the case of **1**, even upon long acquisition time.

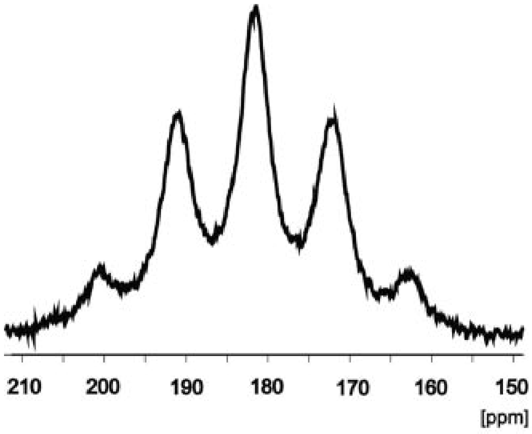


Figure 2. ^{63}Cu NMR spectrum of **2** in D_2O (or **1** after addition of NaOH).

Hence in our systems, protonation of PTA appears to have a marked effect on the rate of that dynamic process in solution and/or on the quadrupolar relaxation of the Cu nuclei in the ^{63}Cu NMR spectroscopy.[14] The significance of distortion from the regular tetrahedral geometry in the solid state[14–16] cannot be ascribed in our case, namely in view of the fluxional behaviour in solution. The effect of the phosphane Tolman cone angle also cannot be recognized in our study since PTA and PTAH are expected to have similar values of the cone angle (103° for PTA[1,17] is a relatively small value in comparison with those of common organophosphane ligands). This differs from other systems for which the type of $^{31}P\{^{1}H\}$ NMR spectrum was associated with the Tolman angle. For example, as for complex **1** (in spite of its small PTAH cone angle), a broad singlet was observed in the $^{31}P\{^{1}H\}$ NMR spectrum (without reporting any ^{63}Cu NMR signal) of $[Cu(PPh_3)_4][BF_4]$[15] bearing a phosphane ligand with a cone angle higher than 136°. However, for $[CuL_4][PF_6]$ (L = PMe_3, PMe_2Ph, PPh_2H, $PPhH_2$)[15] and $[Cu\{P(CH_2OH)_3\}_3\{P(CH_2OH)_2(CH_2O^-)\}]$,[7b] which also have a distorted geometry of the metal centres but bear phosphane ligands with the Tolman cone angle lower than 136° (as in complex **1**), the characteristic quartet due to the coupling with copper (as in complex **2** but not in **1**) was detected. The chemical shift ($\delta = 181.5$ ppm) observed in the ^{63}Cu NMR spectrum of **2** is comparable to those reported for other tetrahedral Cu^{I} complexes, for example, $[Cu(PMePh_2)_4][BF_4]$ ($\delta = 192$ ppm),[15] while $^{1}J_{P-Cu}$ (761 Hz) is also close to the values of 796 and 785 Hz found for $[Cu(PMe_3)_4][PF_6]$ and $[Cu(PMe_2Ph)_4][PF_6]$, respectively, although at different chemical shifts (i.e., $\delta = 287$ and 265 ppm, respectively).[15]

Interestingly, upon changing the pH of the aqueous solution of **1** to a slightly basic value (i.e., pH ≈ 8 after addition of NaOH), one observes in the $^{31}P\{^{1}H\}$ NMR spectrum the conversion of the singlet (Figure 1, **a**) to the 1:1:1:1 quartet of **2** (Figure 1, **d**), in agreement with the deprotonation of **1** to afford **2** (Scheme 1, **b**). A corresponding feature is revealed by the ^{63}Cu NMR spectrum (Figure 2) which shows the appearance of the 1:4:6:4:1 quintet of **2**. The conversion of **1** into **2** can also be monitored by ^{1}H NMR spectroscopy which displays an upfield shift of the NCH_2N protons.

Elemental analyses agree with the proposed formulations of **1** and **2** which are authenticated by single-crystal X-ray diffraction studies, as discussed now.

X-ray Crystal Structures

The asymmetric unit of **1** consists of the $[Cu(PTAH)_4]^{5+}$ cation bearing a +5 charge (due to the protonated character of all the phosphane ligands), which is balanced by five nitrate ions. A thermal ellipsoid plot of the cationic part of **1** is depicted in part (**a**) of Figure 3. The nearly tetrahedral coordination environment about the copper centre is filled by four phosphorus atoms with the corresponding P–Cu–P

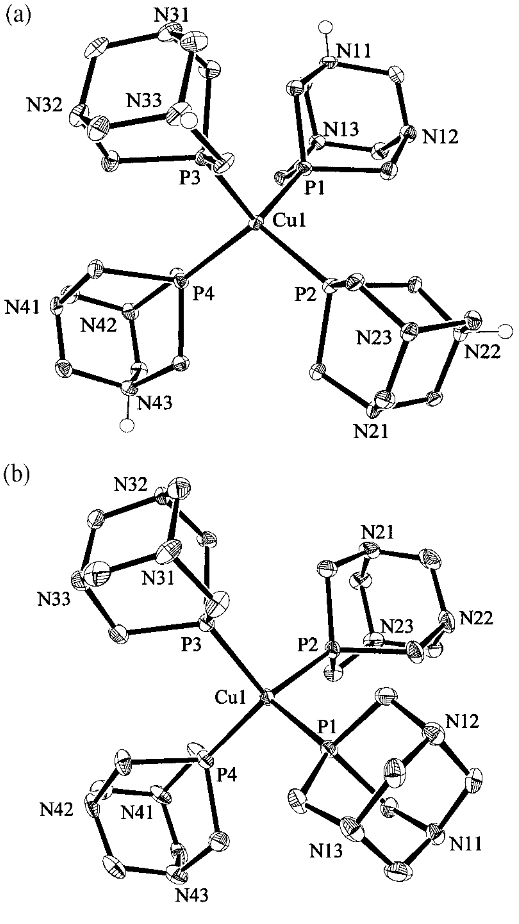


Figure 3. Thermal ellipsoid plots of the cationic parts of **1** (**a**) and **2** (**b**) with a partial labelling scheme. The methylene hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by circles of arbitrary radii.

angles ranging from 108.14(3) to 111.21(3)° [the average value of 109.46(3)° is very close to that of a regular tetrahedron], with an average P···P separation of ca. 3.752 Å. The Cu–P bonds display almost equal, within 3σ, distances [i.e., 2.298(1) Å, average value] (Table 1) which correlate with those reported for other Cu^I complexes bearing four monodentate phosphane ligands, for example, $[Cu\{P(CH_2OH)_3\}_3\{P(CH_2OH)_2(CH_2O^-)\}]$,[7b] $[Cu(PMe_3)_4]X$ {X = Cl,[18] Br,[18] I,[18] $[CuCl_2]^-$[19] or $[CuMe_2]^-$[20]} and $[Cu\{PH_2(mes)\}_4][PF_6]$ (mes = mesityl).[21] In **1**, all the 1,3,5-triaza-7-phosphaadamantane ligands possess a similar geometry and are protonated at one of the nitrogen atoms (i.e., N11, N22, N33 and N43) of each PTAH moiety (Figure 3, **a**), thus resulting in a slight elongation of the (H)N–C bonds [1.519(4) Å, average value] relative to other N–C distances [1.463(4) Å, average value] concerning the unprotonated nitrogen atoms (Table 1). Similar features of the (H)N–C bond elongation were reported for other transition-metal complexes with PTAH ligands.[22] Each NH proton of **1** is further involved in two hydrogen-bonding contacts with nitrate ions, with N···O distances ranging from 2.795(3) to 3.103(3) Å [2.940(3) Å, average value] and N–H···O angles from 122(2) to 177(2)° [142(3)°, average value] (Figure 4). In general, most of the bonding parameters do not significantly differ from the expected values found for related tetrahedral-type transition-metal PTAH/PTA complexes, for example, $[M(PTAH)]Cl_4$ (M = Pt, Pd, Ni),[22a] $[Pt(PTA)_2(PTAH)_2][BF_4]$,[12] $[Pt(PTA)_3(PTAH)]Cl$,[12] $[Au(PTA)(PTAH)_3][PF_6]_4$[22b] and $[Au(PTA)_4]X$ (X = Cl,[22b,23] PF_6[22b]).

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**.

	1	2
Cu1–P1	2.2971(7)	2.2870(15)
Cu1–P2	2.2917(8)	2.2806(16)
Cu1–P3	2.2958(9)	2.2863(15)
Cu1–P4	2.3083(8)	2.2832(15)
P–C	1.856(3)[a]	1.851(6)[a]
(H)N–C	1.519(4)[a]	–
N–C	1.463(4)[b]	1.470(7)[c]
P1–Cu1–P2	111.21(3)	105.90(6)
P1–Cu1–P3	109.46(3)	107.38(5)
P1–Cu1–P4	108.63(3)	113.57(6)
P2–Cu1–P3	110.24(3)	109.57(6)
P2–Cu1–P4	109.08(3)	111.10(6)
P3–Cu1–P4	108.14(3)	109.18(6)

[a] Average distance calculated from 12 bonds. [b] Average distance calculated from 24 bonds. [c] Average distance calculated from 36 bonds.

The crystal structure of **2** bears the $[Cu(PTA)_4]^+$ cation (Figure 3, **b**) with all the phosphane ligands being unprotonated and one nitrate anion balancing the overall charge. The tetrahedral environment around the copper atom is slightly more distorted than that of **1**, exhibiting higher deviations from the idealized geometry, with the minimal and maximal P–Cu–P angles of 105.90(6) and 113.57(6)°, respectively (Table 1). Although the structure of **2**, with mostly similar bonding parameters, resembles that of **1** and therefore is not discussed in detail, it is noteworthy to mention the different geometric arrangements of the phosphane ligands in these compounds (Figure 3).

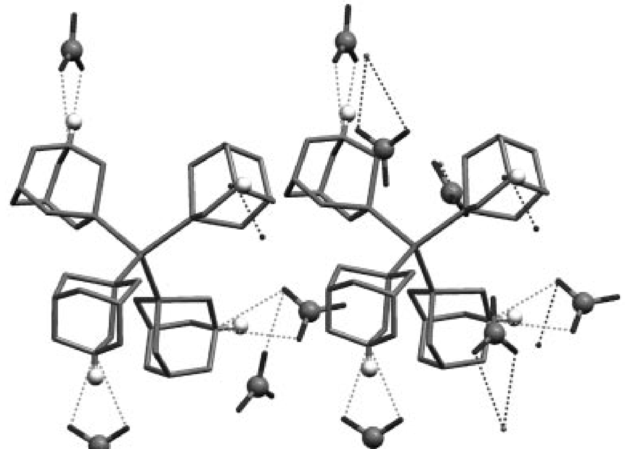


Figure 4. Fragment of the crystal packing diagram of **1** showing the N–H···O hydrogen bonds (dashed lines). NH hydrogen atoms and nitrate nitrogen atoms are shown as white and grey balls, respectively. The methylene hydrogen atoms are omitted for clarity.

Hence, in **1** all the PTAH ligands show nearly equivalent arrangements if viewed along the P–Cu bond (Figure 5, **a**), where the three nitrogen atoms of each PTAH ligand are oriented similarly in relation to the other phosphane ligands forming coplanar P∩N,P sets. In contrast, in compound **2** the PTA ligands are not geometrically equivalent and are arranged in different ways (see parts **b** and **c** in Figure 5) from that in **1** (Figure 5, **a**). Thus, two of the phosphane ligands in **2**, that is, P1 and P4, if viewed down the P–Cu bond are ca. 45° (Figure 5, **b**) and 15° (Figure 5, **c**) rotated, respectively, relative to the orientation of PTAH ligands in **1** (Figure 5, **a**), whereas the other two phosphane ligands (i.e., P2 and P3) are less rotated (ca. 5–8°) approaching the arrangement depicted in part **a** of Figure 5. The analysis of previously reported X-ray crystal structures[6] of a dozen compounds with the $[M(L)_4]$ (L = PTA, PTAH or *N*-methyl-1,3,5-triaza-7-phosphaadamantane) unit reveals that the most common phosphane arrangement is that depicted in part **b** of Figure 5 (i.e., observed in 11 compounds, 3 of them also having 1 phosphane moiety arranged as in

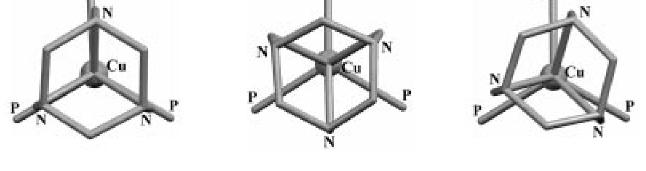


Figure 5. Ball-and-stick partial representation of the X-ray crystal structures of **1** (a) and **2** (b, c) down the P3–Cu1 (a), P1–Cu1 (b) and P4–Cu1 (c) bonds, showing the perspective arrangement of one PTAH/PTA ligand (to which belong the three represented nitrogen atoms) relative to the copper centre and the other phosphane ligands (only the Cu–P bonds are shown). Hydrogen atoms are omitted for clarity.

Figure 5, **c**). Only one compound, $[Au(PTA)(PTAH)_3][PF_6]_4$,[22b] possesses a phosphane arrangement similar to **1** (Figure 5, **a**), whereas there are no examples (apart from **2**) of compounds exhibiting the combination of three types of geometries close to those depicted in parts **a**–**c** of Figure 5.

Conclusions

We have found a simple route to new Cu^I complexes with 1,3,5-triaza-7-phosphaadamantane ligands based on a redox reaction of a Cu^{II} salt with free PTA in aqueous solution at room temperature, thus showing that the reducing ability of PTA[12] can be also extended to copper(II) centres.

Protonation of ligated PTA promotes the ligand exchange and has a drastic effect on both the $^{31}P\{^1H\}$- and ^{63}Cu NMR spectra, with loss of the detection of $^1J_{P-Cu}$ coupling. The recognition of this NMR dependence on the solution pH is of significance towards the NMR characterization of further Cu^I–PTA complexes. The lack of a NMR resonance in spectra of samples obtained in acidic medium could have been a difficulty encountered by others, preventing the characterization and report of Cu complexes with such phosphane ligands, prior to the current study.

The enhanced lability of the PTA ligand upon protonation can be of synthetic value and deserves to be further explored for the preparation of derived complexes.

The obtained Cu^I compounds **1** and **2** show, in the solid state, unusual relative orientations of the PTA (or PTAH) ligands.

The study also shows that it is possible to conveniently prepare Cu complexes bearing PTA (or its protonated form) ligands, allowing the expansion of the still limited group of water-soluble copper phosphane complexes, which encourages the search for their possible applications in aqueous media.

The extension of the work towards the synthesis of Cu compounds with *N*-alkylated PTA derivatives as well as the catalytic activity tests of Cu–PTA species in aqueous medium are currently in progress and will be reported elsewhere.

Experimental Section

General Materials and Experimental Procedures: All chemicals were obtained from commercial sources and used as received. 1,3,5-Triaza-7-phosphaadamantane (PTA) was prepared by a published method.[24] C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined with a Kofler Table. The FAB-MS(+) spectra were obtained with a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (*m*-NBA) matrices of the samples with 8 keV (ca. 1.18×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–400 cm^{-1}) were recorded with a BIO-RAD FTS 3000MX instrument in KBr pellets. ^1H-, $^{13}C\{^1H\}$-, $^{31}P\{^1H\}$- and ^{63}Cu NMR spectra were measured with a Varian UNITY 300 spectrometer at ambient temp. The ^{31}P and ^{63}Cu chemical shifts are relative to an external 85% H_3PO_4 aqueous solution and an [D$_3$]MeCN solution of $[Cu(MeCN)_4][PF_6]$,[14] respectively.

$[Cu(PTAH)_4](NO_3)_5$ (1): To an aqueous solution (10.0 mL) of $Cu(NO_3)_2\cdot 2.5H_2O$ (232 mg, 1.00 mmol) were added concentrated HNO_3 (65% in H_2O, 277 µL, 4.00 mmol) and an excess of an aqueous solution (5.00 mL) of PTA (786 mg, 5.00 mmol) with continuous stirring at room temp. The resulting white suspension was stirred for 1 h, followed by the addition of EtOH (15.0 mL) to provide further precipitation of the product. This was filtered off, washed with EtOH (3×10 mL) and dried in vacuo to afford complex **1** as a white microcrystalline solid. Yield: 92% (926 mg), based on copper nitrate. Complex **1** is slightly soluble in H_2O ($S_{25\,°C} \approx$ 6 mg mL^{-1}) and Me_2CO, is soluble in DMSO and is insoluble in EtOH, MeOH, C_6H_6, $CHCl_3$, CH_2Cl_2 and MeCN. M.p. ca. 215 °C. $C_{24}H_{52}CuN_{17}O_{15}P_4$ (1006.2): calcd. C 28.65, H 5.21, N 23.66; found C 28.64, H 5.59, N 23.35. FAB-MS(+) (*m*-NBA): *m/z* = 816 $[Cu(PTA)_4 + 2Cu - 3H]^+$, 691 $[Cu(PTA)_4]^+$, 659 $[Cu(PTA)_3 + 2Cu - 3H]^+$, 597 $[Cu(PTA)_3 + Cu]^+$, 534 $[Cu(PTA)_3]^+$, 502 $[Cu(PTA)_2 + 2Cu - 3H]^+$, 440 $[Cu(PTA)_2 + Cu]^+$, 377 $[Cu(PTA)_2]^+$, 220 $[Cu(PTA)]^+$, 63 $[Cu]^+$. IR (KBr): $\tilde{\nu}$ = 2984 (br. s) ν(NH + CH), 1382 (br. vs) ν(NO_3), 1120 (m), 1131 (s), 988 (s), 955 (s), 854 (m), 813 (m), 774 (s), 708 (w), 648 (w), 611 (w), 560 (s), 482 (w) and 449 (m) (PTA bands) cm^{-1}. ^1H NMR (300 MHz, D_2O, Me_4Si): δ = 4.74 H^A and 4.87 H^B ($^2J_{AB}$ = 7.0 Hz, 24 H, NCH^AH^BN$^+$ and NCH^AH^BN), 4.18 (br. d, $^2J_{P-H}$ = 4.8 Hz, 24 H, PCH_2N) ppm. ^1H NMR (300 MHz, [D$_6$]dmso, Me_4Si): δ = 4.79 (br. s, 24 H, NCH_2N), 4.11 (br. s, 24 H, PCH_2N) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, D_2O, Me_4Si): δ = 73.8 (br. s, NCH$_2$N), 53.1 (br. s, PCH$_2$N) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, D_2O, 85% H_3PO_4): δ = –82.5 (br. s) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, [D$_6$]dmso, 85% H_3PO_4): δ = –82.6 (br. s) ppm. X-ray-quality single crystals were grown by slow evaporation, in air at room temp., of the reaction filtrate or H_2O solution of **1**.

$[Cu(PTA)_4](NO_3)\cdot 2H_2O$ ($2\cdot 2H_2O$). Method 1: An aqueous cloudy solution (20 mL) of **1** (211 mg, 0.210 mmol) was neutralized by an aqueous 0.168 M NaOH solution (5.0 mL, 0.840 mmol) for 10 min, followed by evaporation of the obtained clear colourless solution in vacuo. The resulting white solid was treated with hot MeOH (ca. 40 mL) to produce a cloudy solution, which was filtered off. The obtained colourless filtrate was left in a fridge at ca. 5 °C for 2 d to afford compound $\mathbf{2}\cdot 2H_2O$ as a white crystalline solid, which was isolated by filtration. Yield: 57% (95 mg), based on **1**. Complex **2** is soluble in H_2O ($S_{25\,°C} \approx$ 64 mg mL^{-1}), DMSO, MeOH and EtOH, is sparingly soluble in THF and Me_2CO and is insoluble in nonpolar solvents. M.p. ca. 245 °C. $C_{24}H_{52}CuN_{13}O_5P_4$ (790.20): calcd. C 36.48, H 6.63, N 23.04; found C 36.55, H 6.80, N 22.42. FAB-MS(+) (*m*-NBA): *m/z* = 816 $[Cu(PTA)_4 + 2Cu - 3H]^+$, 691 $[Cu(PTA)_4]^+$, 534 $[Cu(PTA)_3]^+$, 377 $[Cu(PTA)_2]^+$, 220 $[Cu(PTA)]^+$. IR (KBr): $\tilde{\nu}$ = 3400 (br. s) and 3233 (br. s) ν(H_2O), 2902 (br. s) ν(CH), 1363 (br. s) ν(NO_3), 1243 (m), 1105 (m), 1014 (s), 974 (s), 807 (m) (PTA bands) cm^{-1}. ^1H NMR (300 MHz, D_2O, Me_4Si): δ = 4.61 H^A and 4.58 H^B ($^2J_{AB}$ = 13.5 Hz, 24 H, NCH^AH^BN$^+$ and NCH^AH^BN), 4.14 (br. s, 24 H, PCH_2N) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, D_2O, Me_4Si): δ = 73.8 (br. s, NCH$_2$N), 53.1 (br. s, PCH$_2$N) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, D_2O, 85% H_3PO_4): δ = –78.2 (br. q, $^1J_{^{63}Cu-^{31}P}$ = 761 Hz) ppm. ^{63}Cu NMR (79.5 MHz, D_2O, $[Cu(MeCN)_4][PF_6]$): δ = 181.5 (br. quint, $^1J_{^{63}Cu-^{31}P}$ = 761 Hz) ppm. X-ray-quality crystals of $\mathbf{2}\cdot 2MeOH$ were grown by slow evaporation of the filtrate (left after isolation of **2**) in conical tubes in air for several days.

Method 2: To the blue ethanol solution (30.0 mL) of $Cu(NO_3)_2\cdot 2.5H_2O$ (79 mg, 0.34 mmol) was added an excess of solid PTA (321 mg, 2.04 mmol). The obtained mixture was refluxed for 1 h under dinitrogen, leading to a pale-green suspension. The solid was filtered off, washed with cold EtOH (2×30 mL) and $CHCl_3$

(2 × 15 mL) (to remove the excess phosphane and the formed phosphane oxide) and dried in vacuo to afford complex **2** as a white powder. Yield: 83 % (209 mg), based on copper nitrate.

Refinement Details for the X-ray Crystal Structure Analysis of 1 and 2: Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite-monochromated Mo-K_α radiation. Data were collected at 150 K using omega scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS. Structures were solved by direct methods by using the SHELXS-97 package[25] and refined with SHELXL-97[26] with the WinGX graphical user interface.[27] All hydrogen atoms were inserted in calculated positions. Least square refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms (except for C2 in a methanol molecule in **2** which was refined isotropically) and isotropic for the remaining atoms gave R_1 = 0.0357 (for **1**) and 0.0569 (for **2**). In **2**, the maximum and minimum peaks in the final difference electron density map are 1.704 and –0.933 e Å^{-3}, respectively, close to one of the methanol molecules of crystallization (C2–O2) possibly indicating a disorder which, however, could not be modulated. The selected bonding parameters for **1** and **2** are given in Table 1, and the crystallographic data is summarized in Table 2.

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

	1	**2**·2MeOH
Empirical formula	$C_{24}H_{52}CuN_{17}O_{15}P_4$	$C_{26}H_{56}CuN_{13}O_5P_4$
Formula weight	1006.25	818.26
Temperature [K]	150(2)	150(2)
λ [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	*Cc*	$P2_1/c$
a [Å]	14.1077(14)	12.3982(19)
b [Å]	13.9568(13)	12.4093(19)
c [Å]	20.206(2)	23.181(3)
α [°]	90	90
β [°]	92.508(4)	95.474(4)
γ [°]	90	90
V [Å^3]	3974.6(7)	3550.1(9)
Z	4	4
$\rho_{calcd.}$ [mg m^{-3}]	1.682	1.531
μ(Mo-K_α) [mm^{-1}]	0.800	0.853
No. of collected reflections	15992	23796
No. of unique reflections	8817	5899
R_{int}	0.0369	0.1193
Final R_1,[a] wR_2[b] [$I \geq 2\sigma$]	0.0357, 0.0706	0.0569, 0.1241
GOF on F^2	1.001	0.973

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

CCDC-629755 (for **1**) and -629756 (for **2**) contain the supplementary crystallographic data 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.

Acknowledgments

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, grants BPD/28729/06 and BPD/20869/04, and FCT/POCI 2010 programme (the latter founded by FEDER) as well as by the Human Resources and Mobility Marie Curie Research Training Network (AQUACHEM project, CMTN-CT-2003-503864).

---

[1] For recent review, see: A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, *Coord. Chem. Rev.* **2004**, *248*, 955, and references therein.

[2] a) F. Joó, *Aqueous Organometallic Catalysis*, Kluwer Academic Publishers, Dordrecht, **2001**; b) B. Cornils, W. A. Herrmann (Eds.), *Aqueous Phase Organometallic Catalysis*, Wiley-VCH, Weinheim, **1998**; c) I. T. Horvath, F. Joó (Eds.), *Aqueous Organometallic Chemistry and Catalysis*, NATO ASI Series 3/5, Kluwer Academic Publishers, Dordrecht, **1995**.

[3] a) C. Scolaro, T. J. Geldbach, S. Rochat, A. Dorcier, C. Gossens, A. Bergamo, M. Cocchietto, I. Tavernelli, G. Sava, U. Rothlisberger, P. J. Dyson, *Organometallics* **2006**, *25*, 756; b) C. Scolaro, A. Bergamo, L. Brescacin, R. Delfino, M. Cocchietto, G. Laurenczy, T. J. Geldbach, G. Sava, P. J. Dyson, *J. Med. Chem.* **2005**, *48*, 4161; c) B. Serli, E. Zangrando, T. Gianferrara, C. Scolaro, P. J. Dyson, A. Bergamo, E. Alessio, *Eur. J. Inorg. Chem.* **2005**, 3423.

[4] a) F. Mohr, S. Sanz, E. R. T. Tiekink, M. Laguna, *Organometallics* **2006**, *25*, 3084; b) F. Mohr, E. Cerrada, M. Laguna, *Organometallics* **2006**, *25*, 644.

[5] a) P. Smoleński, F. P. Pruchnik, Z. Ciunik, T. Lis, *Inorg. Chem.* **2003**, *42*, 3318; b) F. P. Pruchnik, P. Smoleński, *Appl. Organomet. Chem.* **1999**, *13*, 829; c) F. P. Pruchnik, P. Smoleński, K. Wajda-Hermanowicz, *J. Organomet. Chem.* **1998**, *570*, 63; d) F. P. Pruchnik, P. Smoleński, E. Gałdecka, Z. Gałdecki, *New J. Chem.* **1998**, *22*, 1395; e) F. P. Pruchnik, P. Smoleński, E. Gałdecka, Z. Gałdecki, *Inorg. Chim. Acta* **1999**, *293*, 110; f) F. P. Pruchnik, P. Smoleński, I. Raksa, *Pol. J. Chem.* **1995**, *69*, 5.

[6] For example, see the Cambridge Structural Database (CSD); F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380.

[7] a) F. Tisato, F. Refoso, G. Bandoli, G. Pilloni, B. Corain, *Inorg. Chem.* **2001**, *40*, 1394; b) D. S. Bharathi, M. A. Sridhar, J. S. Prasad, A. G. Samuelson, *Inorg. Chem. Commun.* **2001**, *4*, 490; c) C. Marzano, M. Pellei, S. Alidori, A. Brossa, G. G. Lobbia, F. Tisato, C. Santini, *J. Inorg. Biochem.* **2006**, *100*, 299.

[8] K. Fisher, I. Dance, G. Willett, *Polyhedron* **1997**, *16*, 2731.

[9] For recent examples, see: a) A. D. Phillips, S. Bolano, S. S. Bosquain, J. C. Daran, R. Malacea, M. Peruzzini, R. Poli, L. Gonsalvi, *Organometallics* **2006**, *25*, 2189; b) F. Mohr, L. R. Falvello, M. Laguna, *Eur. J. Inorg. Chem.* **2006**, 3152; c) B. J. Frost, C. M. Bautista, R. C. Huang, J. Shearer, *Inorg. Chem.* **2006**, *45*, 3481; d) A. Romerosa, T. Campos-Malpartida, C. Lidrissi, M. Saoud, M. Serrano-Ruiz, M. Peruzzini, J. A. Garrido-Cardenas, F. Garcia-Maroto, *Inorg. Chem.* **2006**, *45*, 1289; e) B. J. Frost, S. B. Miller, K. O. Rove, D. M. Pearson, J. D. Korinek, J. L. Harkreader, C. A. Mebi, J. Shearer, *Inorg. Chim. Acta* **2006**, *359*, 283; f) C. Lidrissi, A. Romerosa, M. Saoud, M. Serrano-Ruiz, L. Gonsalvi, M. Peruzzini, *Angew. Chem. Int. Ed.* **2005**, *44*, 2568; g) R. Mejia-Rodriguez, D. Chong, J. H. Reibenspies, M. P. Soriaga, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2004**, *126*, 12004.

[10] a) Y. Y. Karabach, A. M. Kirillov, M. F. C. Guedes da Silva, M. N. Kopylovich, A. J. L. Pombeiro, *Cryst. Growth Des.* **2006**, *6*, 2200; b) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, E. Y. Karabach, M. Haukka, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Adv. Synth. Catal.* **2006**, *348*, 159; c) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, M. Haukka, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Angew. Chem. Int. Ed.* **2005**, *44*, 4345.

[11] a) K. H. Jogun, J. J. Stezowski, E. Fluck, J. Weidlein, *Phosphorus Sulfur* **1978**, *4*, 199; b) R. E. Marsh, M. Kapon, S. Hu, F. H. Herbstein, *Acta Crystallogr., Sect. B* **2002**, *58*, 62.

[12] D. J. Darensbourg, J. B. Robertson, D. L. Larkins, J. H. Reibenspies, *Inorg. Chem.* **1999**, *38*, 2473.

[13] R. Schibli, K. V. Katti, W. A. Volkert, C. L. Barnes, *Inorg. Chem.* **1998**, *37*, 5306.

[14] I. Szymanska, *Pol. J. Chem.* **2006**, *80*, 1095.

[15] J. R. Black, W. Levason, M. D. Spicer, M. Webster, *J. Chem. Soc., Dalton Trans.* **1993**, 3129.
[16] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.
[17] C. A. McAuliffe, in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, New York, **1987**, vol. 2, chapter 14, pp. 1016–1017.
[18] G. A. Bowmaker, P. C. Healy, L. M. Engelhardt, J. D. Kildea, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1990**, *43*, 1697.
[19] K.-M. Chi, J. Farkas, M. J. Hampden-Smith, T. T. Kodas, E. N. Duesler, *J. Chem. Soc., Dalton Trans.* **1992**, 3111.
[20] D. F. Dempsey, G. S. Girolami, *Organometallics* **1988**, *7*, 1208.
[21] I. V. Kourkine, S. V. Maslennikov, R. Ditchfield, D. S. Glueck, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, *Inorg. Chem.* **1996**, *35*, 6708.
[22] a) D. J. Darensbourg, T. J. Decuir, N. W. Stafford, J. B. Robertson, J. D. Draper, J. H. Reibenspies, A. Katho, F. Joó, *Inorg. Chem.* **1997**, *36*, 4218; b) J. M. Forward, Z. Assefa, R. J. Staples, J. P. Fackler Jr, *Inorg. Chem.* **1996**, *35*, 16.
[23] J. M. Forward, D. Bohmann, J. P. Fackler Jr, *Z. Kristallogr.* **1996**, *211*, 485.
[24] a) D. J. Daigle, A. B. Pepperman Jr, S. L. Vail, *J. Heterocycl. Chem.* **1974**, *11*, 407; b) D. J. Daigle, *Inorg. Synth.* **1998**, *32*, 40.
[25] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[26] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**.
[27] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

Received: December 6, 2006