New water-soluble azido- and derived tetrazolato-platinum(II) complexes with PTA. Easy metal-mediated synthesis and isolation of 5-substituted tetrazoles†

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The water-soluble four- and five-coordinate diazido-platinum(II) complexes *cis*-$[Pt(N_3)_2(PTA)_2]$ (**1**) (PTA = 1,3,5-triaza-7-phosphaadamantane), *cis*-$[Pt(N_3)_2(Me\text{-}PTA)_2]I_2$ (**2**) (Me-PTA = *N*-methyl-1,3,5-triaza-7-phosphaadamantane cation) and $[Pt(N_3)_2(PTA)_3]$ (**3**) were obtained by reactions of *cis*-$[Pt(N_3)_2(PPh_3)_2]$ with PTA or [Me-PTA]I in dichloromethane. [2 + 3] cycloadditions of **1** with organonitriles NCR gave the bis(tetrazolato) complexes *trans*-$[Pt(N_4CR)_2(PTA)_2]$ (R = Ph (**4**), 4-ClC_6H_4 (**5**) or 3-NC_5H_4 (**6**)), the reactions being greatly accelerated by microwave irradiation. 5-R-1H-Tetrazoles N_4CR (R = Ph, 4-ClC_6H_4 and 3-NC_5H_4) were easily liberated from the tetrazolato complexes **4–6** and isolated in high yields, in a single-pot process, upon reaction with aqueous diluted HCl, with concomitant formation of the water soluble *cis*-$[Pt(Cl)_2(PTA\text{-}H)_2]$ complex **7**. Alternatively, in a less convenient method, the tetrazoles could be liberated on reaction of **4–6** with propionitrile which also leads to the dicyano *trans*-$[Pt(CN)_2(PTA)_2]$ complex **8**. The compounds were characterized by IR, ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopies, FAB^+-MS or ESI-MS, elemental analyses and (for **1** and **4**) also by X-ray diffraction.

Introduction

In view of the wide applications and pharmacological interest of N-containing heterocycles, the chemistry of tetrazoles and their complexes, in particular, has received a good attention.[1] A variety of tetrazole compounds was obtained by cycloaddition reactions of organonitriles or isocyanides with azido ligands at Group 10 metals.[2] Namely, the reactions of various nitriles with the diazidoplatinum(II) complex *cis*-$[Pt(N_3)_2(PPh_3)_2]$, investigated by Fehlhammer *et al.*,[3] gave the corresponding bis(tetrazolato) complexes *trans*-$[Pt(N_4CR)_2(PPh_3)_2]$. However, among the several synthetic methods reported so far, most of them have some drawbacks like drastic reaction conditions, water sensitivity and presence of highly toxic, explosive and volatile hydrazoic acids.[4] Sharpless *et al.*[5] improved the method by using a zinc salt as a Lewis acid promoter and performing the reactions in aqueous media. Amantini *et al.*[6] efficiently synthesized tetrazoles by the addition of trimethylsilyl azide to organic nitriles using tetrabutylammonium fluoride as catalyst. Nevertheless, reduction of the reaction time and temperature and isolation of the final product by an easy and convenient way usually remain challenging issues.

Some of us recently showed[7] that microwave irradiation promotes the [2 + 3] cycloaddition of organonitriles with azide, resulting in a shortening of the reaction time relatively to the conventional heating and eventually in a higher selectivity. To explore further our previous studies in this arena towards the synthesis and isolation of 5-substituted-1H-tetrazoles in environment-friendly conditions, the use of the hydrophilic 1,3,5-triaza-7-phosphaadamantane (PTA, Fig. 1) instead of the hydrophobic PPh_3 has been taken into account as a promising alternative. The coordination chemistry of this aqua-soluble phosphine and derived species has received an increased interest in recent years,[8] in view of the good solubility of transition metal PTA complexes in water, thus making possible their efficient application in aqueous phase catalysis,[8–10] as water-soluble antitumor agents[8,11–13] and photoluminescent materials.[8,14–15] In the last years a few new complexes of platinum(II) and PTA have been tested as catalysts, *e.g.* *cis*-$[PtX_2(PTA)_2]$ (X = Cl, Br, I),[16] and in biological activity studies, *e.g.* (*SP*-4,2)-[PtCl(8-MTT)(PPh_3)(PTA)] and *cis*-$[Pt(8\text{-}MTT)_2(PPh_3)(PTA)]$ [8-MTT = 8-(methylthio)theophylline].[17] Equilibrium constants for the formation of $[PtX(PTA)_3]^+$ were also investigated by reacting $[PtCl(PTA)_3]Cl$ with various halides and pseudohalides (X = Br^-, N_3^-, NCS^-, and I^-),[18] and the structural characterization of the unusual five-coordinate distorted square pyramidal Pt(II) complex $[PtI_2(PTA)_3]$ was also presented.[19]

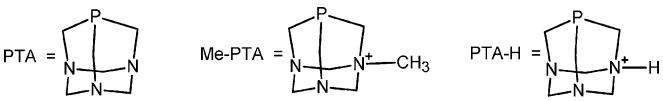

Fig. 1 Structures of PTA and the derived alkylated (Me-PTA) and protonated (PTA-H) species.

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We now report the synthesis of the new water-soluble four- and five-coordinate diazido-platinum(II) complexes *cis*-$[Pt(N_3)_2(PTA)_2]$ (**1**), *cis*-$[Pt(N_3)_2(Me\text{-}PTA)_2]I_2$ (**2**) (Me-PTA = *N*-methylated-PTA, Fig 1) and $[Pt(N_3)_2(PTA)_3]$ (**3**), as well as of the bis(tetrazolato) compounds *trans*-$[Pt(N_4CR)_2(PTA)_2]$ [R = Ph (**4**), 4-ClC_6H_4 (**5**) and 3-NC_5H_4 (**6**)], derived from [2 + 3] cycloaddition of NCR with **1**, the reaction being accelerated by microwave irradiation. We have also found an easy and convenient way to liberate the ligated 5-R-1H-tetrazoles upon treatment of the complexes with an aqueous 0.1 M HCl solution, which provides a particularly promising method in view of the good solubility of the complex product *cis*-$[Pt(Cl)_2(PTA\text{-}H)_2]Cl_2$ in water, in contrast with tetrazoles, what greatly facilitates their separation.

All complexes were characterized by IR, ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopies, FAB$^+$-MS (positive fast atom bombardment mass spectrometry, elemental analyses and (for **1** and **4**) also by X-ray structural analysis.

Experimental

Warning!

Much care should be taken when working with azides, especially when heating, as they are potentially explosive compounds.

General materials and experimental procedures

All manipulations were done under an inert atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques. All solvents were dried, degassed and distilled prior to use. $K_2[PtCl_4]$ (Aldrich), was used as received. 1,3,5-Triaza-7-phosphaadamantane (PTA)[20], *N*-methyl-1,3,5-triaza-7-phosphaadamantane iodide [PTA-Me]I[20] and $[Pt(N_3)_2(PPh_3)_2]$[21] 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. The electrical conductance of the solutions was measured with a SCHOTT CG 855 conductimeter at room temperature. The FAB$^+$-MS spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (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. Electrospray mass spectra of 5-substituted-1H-tetrazoles were carried out with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion (ESI) source. The solutions in dichloromethane were continuously introduced into the mass spectrometer source with a syringe pump at a flow rate of 10 μL min^{-1}. The drying gas temperature was maintained at 350 °C and dinitrogen was used as nebulizer gas at a pressure of 35 psi. Scanning was performed from m/z = 50 to 1500. The compounds were observed in the negative mode (capillary voltage = −4000 V). Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. ^1H, ^{13}C and ^{31}P NMR spectra were measured on a Bruker 300 and 400 UltraShield™ spectrometers at ambient and low temperatures. ^1H and ^{13}C chemical shifts δ are expressed in ppm relative to $Si(Me)_4$ and $\delta(^{31}P)$ relative to 85% H_3PO_4. Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; m, complex multiplet; vt, virtual triplet; br, broad. The microwave irradiation experiments were undertaken in a focused microwave CEM Discover reactor (10 mL, 13 mm diameter, 300 W, 2450 ± 50 MHz) which is fitted with a rotational system and an IR detector of temperature.

Preparation of compounds

***cis*-$[Pt(N_3)_2(PTA)_2]\cdot 0.5CH_2Cl_2$, $1\cdot 0.5CH_2Cl_2$.** To a solution (15.0 mL) of $[Pt(N_3)_2(PPh_3)_2]$ (141 mg, 0.175 mmol) in dichloromethane (15.0 mL), PTA (55.0 mg, 0.350 mmol) was added. The mixture was stirred for *ca.* 1 h under dinitrogen at room temperature. The white precipitate **1** was separated from the colourless solution by filtration, washed with dichloromethane (3 × 10 mL) and dried *in vacuo* to afford complex $\mathbf{1}\cdot 0.5CH_2Cl_2$ as a white microcrystalline solid. Yield of $\mathbf{1}\cdot 0.5CH_2Cl_2$ 83% (93 mg). Complex **1** is soluble in H_2O ($S_{25°C} \approx 2$ mg mL^{-1}), DMSO, MeOH, slightly soluble in EtOH, $CHCl_3$, CH_2Cl_2 and THF and insoluble in C_6H_6. $[Pt(N_3)_2(PTA)_2]\cdot 0.5CH_2Cl_2$, $C_{12.5}H_{25}N_{12}ClP_2Pt$ (635.89): calcd C 23.61, N 26.43 H 3.96; found C 23.60, N 26.29, H 3.98. FAB$^+$-MS: m/z = 593 $[M]^+$, 551 $[M\text{-}(N_3)]^+$, 509 $[M\text{-}(N_3)_2]^+$, 352 $[Pt(PTA)]^+$. Molar conductivity (CH_3NO_2, conc. = 10^{-3} M): Λ_M 0.3 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2924 (s br) ν(CH), 2033 (s br) $\nu(N_3)$, 1448 (m), 1410 (m), 1283 (m), 1242 (s), 1101 (m), 1014 (s), 978 (s), 947 (s), 901 (m), 806 (m), 740 (m), 580 (m) (PTA) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 4.66 H^A and 4.40 H^B (J_{AB} = 13.0 Hz, NCH^AH^BN, 12H), 4.23 (s, PCH_2N, 12H). $^{31}P\{^1H\}$ NMR (121.4 MHz, D_2O): δ = −59.1 (s, J(Pt-P) = 3139 Hz). X-Ray quality single crystals were grown by slow evaporation in air at room temperature of a water solution of **1**.†

***cis*-$[Pt(N_3)_2(Me\text{-}PTA)_2]I_2\cdot CH_2Cl_2$, $2\cdot CH_2Cl_2$.** To a solution of $[Pt(N_3)_2(PPh_3)_2]$ (192 mg, 0.239 mmol) in CH_2Cl_2 (30.0 mL), 20 mL of a MeOH solution of [Me-PTA]I (143 mg, 0.478 mmol) was added. The mixture was stirred for *ca.* 12 h under dinitrogen. The precipitate **2** was separated from the slightly yellow solution by filtration, washed with dichloromethane (3 × 20 mL) and dried *in vacuo* to afford complex **2** as a pale-yellow microcrystalline solid. Yield of $\mathbf{2}\cdot CH_2Cl_2$ 80% (184 mg). Complex **2** is soluble in H_2O, DMSO, MeOH, slightly soluble in EtOH and insoluble in $CHCl_3$, CH_2Cl_2, THF and C_6H_6. $[Pt(N_3)_2(Me\text{-}PTA)_2]I_2\cdot CH_2Cl_2$, $C_{15}H_{32}N_{12}I_2Cl_2P_2Pt$ (962.24): calcd C 18.72, N 17.42, H 3.35; found C 18.45, N 17.39, H 3.42. FAB$^+$-MS: m/z = 835 $[M\text{-}(N_3)]^+$, 793 $[M\text{-}(N_3)_2]^+$, 666 $[Pt(Me\text{-}PTA)_2I]^+$. Molar conductivity (CH_3NO_2, conc. = 10^{-3} M): Λ_M 172 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2960 (s br) ν(CH), 2060 (s br) $\nu(N_3)$, 1452 (m), 1310 (m), 1279 (m), 1121 (m), 1091 (s), 1026 (m), 968 (m), 932 (m), 901 (m), 815 (m), 751 (m), 571 (m) (M-PTA) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 5.15 H^A and 5.05 H^B (J_{AB} = 11.2 Hz, $NCH^AH^BN^+$, 8H), 4.89 (s, PCH_2N^+, 4H), 4.56 H^A and 4.36 H^B (J_{AB} = 11.9 Hz, NCH^AH^BN, 4H), 4.53 H^A and 4.31 H^B (J_{AB} = 12.9 Hz, PCH^AH^BN, 8H), 2.84 (s, CH_3, 6H). $^{31}P\{^1H\}$ NMR (121.4 MHz, DMSO-d_6): δ = −47.2 (s, J(Pt-P) = 3153 Hz).

$[Pt(N_3)_2(PTA)_3]\cdot CH_2Cl_2$, $3\cdot CH_2Cl_2$. To a solution (35.0 mL) of $[Pt(N_3)_2(PPh_3)_2]$ (111 mg, 0.138 mmol) in dichloromethane, PTA (65.0 mg, 0.414 mmol) was added. The cloudy solution was stirred for *ca.* 1 h under dinitrogen at room temperature and the formed colourless solution was taken to dryness *in vacuo*. The residue was washed with diethyl ether (3 × 10 mL) to remove PPh_3 and crystallized from CH_2Cl_2 in a fridge (+4 °C) to afford complex **3** as a white microcrystalline solid. Yield of $\mathbf{3}\cdot CH_2Cl_2$ 58% (67 mg).

Complex **3** is soluble in H_2O, DMSO, MeOH, EtOH, $CHCl_3$ and CH_2Cl_2, sparingly soluble in toluene and insoluble in C_6H_6 and diethyl ether. $[Pt(N_3)_2(PTA)_3]\cdot CH_2Cl_2$, $C_{19}H_{38}N_{15}Cl_2P_3Pt$ (835.51): calcd C 27.31, N 25.15, H 4.58; found C 27.80, N 24.81, H 4.88. FAB$^+$-MS: m/z = 708 $[M]^+$, 606 $[M\text{-}(N_3)]^+$. Molar conductivity (CH_3NO_2, conc. = 10^{-3} M): Λ_M 0.4 Ω^{-1} cm^2 mol^{-1}. IR (KBr): 2926 (s br) ν(CH), 2052 (s br) $\nu(N_3)$, 1441 (m), 1419 (m), 1289 (m), 1243 (m), 1015 (s), 975 (s), 945 (s), 903 (m), 809 (m), 741 (m), 583 (m) (PTA) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.24 (s, PCH_2N, 18H,), 4.33 H^A and 4.24 H^B (J_{AB} = 13.0 Hz, NCH^AH^BN, 18H,). ^{1}H NMR (400 MHz, $CDCl_3$, 213 K): δ = 4.63 (s, PCH_2N, 18H), 4.59 H^A and 4.51 H^B (J_{AB} = 13.0 Hz, NCH^AH^BN, 18H,). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K): unresolved very broad spectrum. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 213 K): δ = −51.6 (t, J(Pt-P) = 3304 Hz, ^2J(P-P) = 23.5 Hz), −57.6 (d, J(Pt-P) = 2187 Hz, ^2J(P-P) = 23.5 Hz).

***trans*-[Pt(N$_4$CPh)$_2$(PTA)$_2$]·0.5PhCN, 4·0.5PhCN.** A mixture of $[Pt(N_3)_2(PTA)_2]\cdot 0.5CH_2Cl_2$ (**1**·0.5CH_2Cl_2) (65.0 mg, 0.10 mmol) and PhCN (5.0 mL, 48.5 mmol) was added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 100 °C. The excess of PhCN was then removed *in vacuo* and the resulting residue was washed repeatedly with 5 mL portions of diethyl ether. Recrystallization from a dichloromethane/diethyl ether mixture gave off-white crystals of *trans*-$[Pt(N_4CPh)_2(PTA)_2]\cdot 0.5PhCN$ (**4**·0.5PhCN) Yield 65% (57 mg). Complex **4** is soluble in DMSO, EtOH, $CHCl_3$, CH_2Cl_2, and insoluble in H_2O, diethyl ether and C_6H_6. *trans*-$[Pt(N_4CPh)_2(PTA)_2]\cdot 0.5PhCN$, $C_{29.5}H_{36.5}N_{14.5}P_2Pt$ (851.2): calcd C 41.62, N 23.86, H 4.32; found C 41.38, N 23.16, H 4.36. FAB$^+$-MS: m/z = 800 $[M]^+$, 654 $[M\text{–}N_4CPh]^+$. IR (KBr): 2931 (s br), 2230 (m), 1615 (m), 1445 (m), 1384 (m), 1280 (m), 1242 (m), 1100 (m), 1014 (s), 973 (s), 803 (m), 735 (m), 583 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18-7.45 (m, 2Ph + 0.5 PhCN, 12.5H), 4.45 (s, NCH_2N, 12H), 4.23 (s, PCH_2N, 12H). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = −56.2 (s, J(Pt-P) = 2497 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$,): δ = 164.3 (s, N_4C), 135.6 (s, 4-C, C_6H_5), 133.6 (s, 4-C, C_6H_5, PhCN), 132.7 (s, 2,6-C, C_6H_5, PhCN), 129.2 (s, 2,6-C, C_6H_5), 128.7 (s, 3,5-C, C_6H_5 PhCN), 127.7 (s, 3,5-C, C_6H_5), 127.4 (s, 1-C, C_6H_5), 113.4 (s, 1-C, C_6H_5, PhCN), 73.2 (vt, ^3J(CP) = 6.0 Hz, N-CH_2-N, PTA), 50.3 (vt, ^1J(CP) = 15.7 Hz, P-CH_2-N, PTA). X-Ray quality single crystals were grown from $CHCl_3$–toluene solution of **4** in air at room temperature.†

***trans*-[Pt{N$_4$C(4-ClC$_6$H$_4$)}$_2$(PTA)$_2$], 5.** A mixture of $[Pt(N_3)_2(PTA)_2]\cdot 0.5CH_2Cl_2$ (**1**·0.5CH_2Cl_2) (65.0 mg, 0.10 mmol), 4-ClC_6H_4CN (138 mg, 1.00 mmol) and DMF (5.0 mL) was added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 °C. The solvent was then removed *in vacuo* and the resulting residue was washed repeatedly with 5 mL portions of diethyl ether. Recrystallization from a dichloromethane–diethyl ether mixture gave off-white crystals of **5**. Yield 60% (53 mg). Complex **5** is soluble in DMSO, MeOH, EtOH, $CHCl_3$, CH_2Cl_2, sparingly soluble in H_2O and insoluble in diethyl ether and C_6H_6. *trans*-$[Pt\{N_4C(4\text{-}ClC_6H_4)\}_2(PTA)_2]$, $C_{26}H_{32}N_{14}C_{12}P_2Pt$ (868.6): calcd C 35.95, N 22.58, H 3.71; found C 36.10, N 22.51, H 3.66. FAB$^+$-MS: m/z = 869 $[M]^+$, 689 $[M\text{–}N_4C(4\text{-}ClC_6H_4)]^+$. IR (KBr): 2933 (s br), 1630 (m), 1440 (m), 1273 (m), 1239 (m), 1096 (m), 1010 (s), 975 (s), 802 (m), 736 (m), 582 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$,): δ = 8.10, 7.48 (2 dd, C_6H_4, ^3J(HH) = 8.7 Hz, ^4J(HH) = 1.32 Hz, 8H), 4.43 (s, NCH_2N, 12H), 4.13 (s, PCH_2N, 12H). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = −56.3 (s, J(Pt-P) = 2491 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$,): δ = 164.3 (s, N_4C), 135.6 (s, 4-C, C_6H_4), 129.2 (s, 2,6-C, C_6H_4), 127.7 (s, 3,5-C, C_6H_4), 127.4 (s, 1-C, C_6H_4), 73.2 (vt, ^3J(CP) = 3.5 Hz, N-CH_2-N, PTA), 50.3 (vt, ^1J(CP) = 9.6 Hz, P-CH_2-N, PTA).

***trans*-[Pt{N$_4$C(3-NC$_5$H$_4$)}$_2$(PTA)$_2$]·0.5CH$_2$Cl$_2$, 6·0.5CH$_2$Cl$_2$.** A mixture of $[Pt(N_3)_2(PTA)_2]\cdot 0.5CH_2Cl_2$ (**1**·0.5CH_2Cl_2) (65.0 mg, 0.10 mmol), 3-NC_5H_4CN (104 mg, 1.00 mmol) and DMF (5.0 mL) was added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 1 h at 125 °C. The solvent was then removed *in vacuo* and the resulting residue was washed repeatedly with 5 mL portions of diethyl ether. Recrystallization from a dichloromethane–diethyl ether mixture gave off-white crystals of **6**·0.5CH_2Cl_2. Yield 58% (50 mg). Complex **6** is soluble in DMSO, MeOH, EtOH, $CHCl_3$, CH_2Cl_2, sparingly soluble in H_2O and insoluble in diethyl ether and C_6H_6. *trans*-$[Pt\{(3\text{-}NC_5H_4)\}_2(PTA)_2]\cdot 0.5CH_2Cl_2$, $C_{24.5}H_{33}N_{16}ClP_2Pt$ (844.11): calcd C 34.86, N 26.55, H 3.94; found C 35.05, N 26.04, H 3.96. FAB$^+$-MS: m/z = 802 $[M]^+$, 656 $[M\text{–}N_4C(3\text{-}NC_5H_4)]^+$. IR (KBr): 2924 (s br), 1621 (m), 1584 (s), 1467 (m), 1413 (m), 1280 (s), 1243 (m), 1096 (m), 1032 (s), 1012 (s), 973 (s), 943 (s), 897 (m), 798 (m), 762 (m), 737 (m) 582 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.42 (dd, H^2, $^4J(H^2H^6)$ = 2.0 Hz, $^5J(H^2H^5)$ = 0.9 Hz, 2H), 8.70 (dd, H^6, $^3J(H^6H^5)$ = 8.0 Hz, $^4J(H^6H^2)$ = 2.0 Hz, 2H), 8.45 (ddd, H^5, $^3J(H^5H^6)$ = 8.0 Hz, $^3J(H^5H^4)$ = 4.9 Hz, $^5J(H^5H^2)$ = 0.9 Hz, 2H), 7.46 (d, H^4, $^3J(H^4H^5)$ = 4.9 Hz, 2H), 4.44 (s, NCH_2N, 12H), 4.16 (s, PCH_2N, 12H). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = −56.2 (s, J(Pt-P) = 2479 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$,): δ = 162.8 (s, N_4C), 150.7 (s, 4-C, py), 149.8 (s, 2-C, py), 134.7 (s, 6-C, py), 124.0 (s, 5-C, py), 73.2 (vt, ^3J(CP) = 3.5 Hz, N-CH_2-N, PTA), 50.4 (vt, ^1J(CP) = 9.6 Hz, P-CH_2-N, PTA).

Method (a) for 5-R-1H-tetrazoles (R = Ph, 4-ClC$_6$H$_4$ or 3-NC$_5$H$_4$) and *cis*-[Pt(Cl)$_2$(PTA-H)$_2$]Cl$_2$ (7). A suspension of *trans*-$[Pt(N_4CR)_2(PTA)_2]$ [**4** (170 mg, 0.20 mmol) or **5** (174 mg, 0.20 mmol) or **6** (169 mg, 0.20 mmol)] in aqueous 0.1 M HCl (15 mL) was refluxed for 0.5 h. The white precipitate formed during the reaction, after separation by filtration, analyzed as the corresponding 5-R-1H-tetrazole (R = Ph, 4-ClC_6H_4 or 3-NC_5H_4) (yields *ca.* 80%). Evaporation to dryness of the filtered reaction solution led to **7** as a off-white solid. $[Pt(Cl)_2(PTAH)_2]Cl_2$, $C_{12}H_{26}C_{l4}N_6P_2Pt$ (653.22): calcd C 22.06, N 12.86, H 4.01; found C 22.54, N 12.67, H 4.63. IR (KBr): 2971 (s br) ν(CH), 1447 (m), 1419 (m), 1303 (m), 1242 (w), 1024 (s), 977 (s), 951 (s), 813 (m), 770 (m), 572 (m) (PTA) cm^{-1}. ^{1}H NMR (400 MHz, D_2O): δ = 4.47 (br s, PCH_2N, NCH_2N and NCH_2N^+, 24 H). ^{31}P{^{1}H} NMR (162.0 MHz, D_2O): δ = −47.9 (s, J(Pt-P) = 3480 Hz).

Method (b) for 5-R-1H-tetrazoles (R = Ph, 4-ClC$_6$H$_4$ or 3-NC$_5$H$_4$) and *trans*-[Pt(CN)$_2$(PTA)$_2$] (8). A solution of *trans*-$[Pt(N_4CR)_2(PTA)_2]$ [**4** (170 mg, 0.20 mmol) or **5** (174 mg, 0.20 mmol) or **6** (169 mg, 0.20 mmol)] in NCEt (15 mL) was refluxed for 36 h whereupon the solvent was removed to half of its volume *in vacuo.* The reaction mixture was left to cool to room temperature and then treated with diethyl ether (15 mL). The white solid of *trans*-$[Pt(CN)_2(PTA)_2]$ **8** was isolated by

filtration, washed with dichloromethane (2 × 5 mL) and dried *in vacuo*. The mother liquor (diethyl ether fraction) was evaporated to dryness and the resulting compound was identified as the corresponding 5-R-1H-tetrazole (R = Ph, 4-ClC_6H_4 or 3-NC_5H_4). The above dichloromethane fractions from washing **8** contained some decomposition products of the platinum complexes, such as PTA oxide and traces of unknown compounds, which were observed by $^{31}P\{^1H\}$ NMR. **8** was crystallized from hot methanol. Yield of **8** *ca.* 60% (70 mg). **8** is soluble in H_2O, DMSO, MeOH, slightly soluble in EtOH, $CHCl_3$, CH_2Cl_2 and insoluble in C_6H_6.

trans-*[Pt(CN)$_2$(PTA)$_2$]*. IR (KBr): 2927 (s br) *ν*(CH), 2127 (m) *ν*(CN), 1442 (m), 1279 (m), 1242 (s), 1013 (s), 1014 (s), 971 (s), 944 (s), 901 (m), 804 (m), 737 (m), 696 (m) (PTA) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 4.62 (s, NCH_2N, 12H), 4.43 (s, PCH_2N, 12H). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_3OD): δ = –64.5 (s, *J*(Pt-P) = 2060 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): δ = 126.9 (s, CN), 72.1 (s, br, N-CH_2-N, PTA), 51.2 (vt, $^1J(CP)$ = 16.0 Hz, P-CH_2-N, PTA).

5-(Ph)-1H-Tetrazole, IR (KBr). 2980 (s br), 2974 (s br), 2955 (s br), 2932 (s br), 1611 (s), 1570 (m), 1450 (m), 1415 (m), 730 (s) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.12 (m, H^2, H^6, 2H), 7.50 (m, H^3, H^5, 2H), 7.45 (m, H^4, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): δ = 154.0 (s, N_4C), 131.6 (s, 4-C, C_6H_5), 129.2 (s, 2,6-C, C_6H_5), 127.0 (s, 3,5-C, C_6H_5), 125.3 (s, 1-C, C_6H_5). ESI-MS: *m*/*z* 145.1 $[M\text{-}H]^-$.

5-(4-ClC$_6$H$_4$)-1H-Tetrazole, IR (KBr). 3096 (m), 3070 (m), 2977 (s br), 2910 (s br), 2850 (s br), 2867 (m), 2832 (m), 1610 (s), 1564 (m), 1436 (s), 1384 (s), 1095 (s), 745 (s), 509 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70, 7.50 (2 m, 4-ClC_6H_4C, 4H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 148.2 (s, N_4C), 132.5 (s, 4-C, C_6H_5), 130.9 (s, 2,6-C, C_6H_5), 128.8 (s, 3,5-C, C_6H_5), 123.8 (s, 1-C, C_6H_5). ESI-MS: *m*/*z* 179.0 $[M\text{-}H]^-$.

5-(3-NC$_5$H$_4$)-1H-Tetrazole, IR (KBr). 3011 (s br), 2983 (s br), 2959 (s br), 1670 (m), 1620 (s), 1561 (s), 1025 (m), 830 (m), 1415 (m), 830 (m), 723 (m) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.1-8.0 (m, H^2 and H^6, 2H), 7.6–7.5 (m, H^4 and H^5, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): δ = 153.2 (s, 4-C, py), 152.6 (s, 2-C, py), 148.2 (s, N_4C), 132.5 (s, 6-C, py), 128.0 (s, 5-C, py). ES-MS: *m*/*z* 146.1 $[M\text{-}H]^-$.

Refinement details for the X-ray crystal structure analysis of 1 and 4†

Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo Kα 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[22] and refined with SHELXL-97[23] with the WinGX graphical user interface.[24] All hydrogens were inserted in calculated positions except those of crystallization water molecules in **1**, which were located in the difference Fourier map. Least-square refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms gave R_1 = 0. 0311 [$I > 2\sigma(I)$; R_1 = 0. 0533 (all data)] for **1**, and the maximum and minimum peaks in the final difference electron density map are of 1.324 and –1.294 e Å^{-3}, close to the platinum atom. For **4** there is disordered solvent in the structure. Attempts were made to model them, but were unsuccessful. PLATON/SQUEEZE[25] was used to correct the data. A potential solvent volume of 273.9 Å^3 was found. 17 electrons per unit cell worth of scattering were located in the void. The stoichiometry was tentatively calculated as 1 water molecule which results in 20 electrons per unit cell. The modified dataset improved the R_1 value by *ca.* 7%; final R_1 = 0.0787. In both structures, the maximum and minimum peaks in the final difference electron density map are located close to the platinum atom.

The selected bonding parameters for **1** and **4** are given in Table 1, and the crystallographic data summarized in Table 2. CCDC reference numbers 688071 & 688072.†

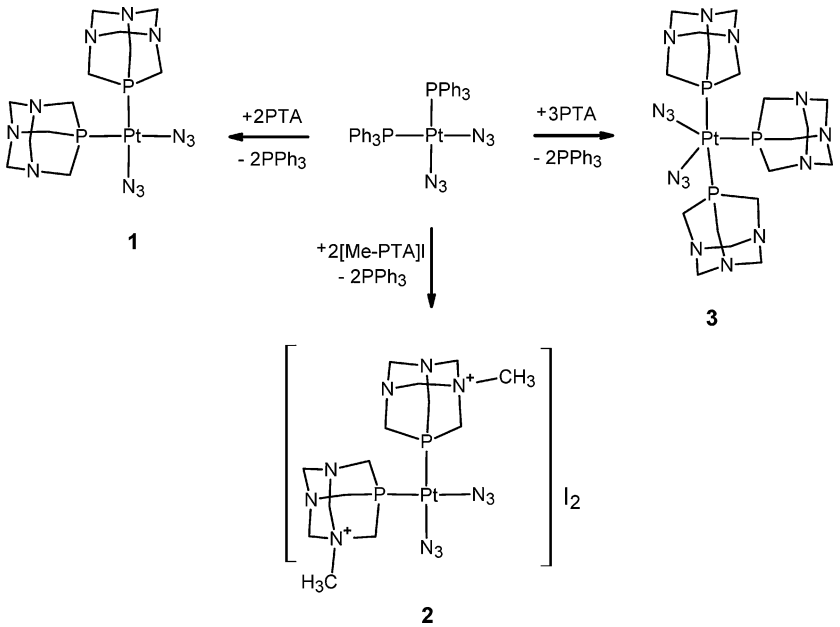
Table 1 Selected bond lengths (Å) and angles (°) for **1** and **4**

	1	**4**
Pt1–P1	2.2305(15)	2.306(4)
Pt1–P2	2.2231(16)	2.311(5)
Pt1–N1	2.074(5)	1.999(12)
Pt1–N4	2.076(5)	—
Pt1–N5	—	2.019(14)
N1–N2	1.208(7)	1.315(17)
N1–N4	—	1.367(17)
N2–N3	1.159(8)	1.363(18)
N4–N5	1.211(7)	—
N5–N6	1.153(8)	—
N5–N6	—	1.382(18)
N5–N8	—	1.286(17)
N6–N7	—	1.315(19)
P1–Pt1–P2	95.56(5)	177.99(13)
N1–Pt1–N5	—	177.9(5)
N1–Pt1–N4	87.8(2)	—
Pt1–N1–N2	121.7(4)	124.9(10)
Pt1–N4–N5	122.1(4)	—
N1–N2–N3	174.2(6)	107.7(11)
N4–N5–N6	174.6(6)	—

Table 2 Hydrogen bonds (Å, °) in **1**[a]

D–H···A	*d*(H···A)	*d*(D···A)	∠(D–H···A)
Between water network			
O1–H1A···O2	1.92	2.758(7)	147.0
O2–H2A···O3^{i}	2.03	2.842(6)	168.0
O3–H3B···O4	2.32	2.868(5)	122.0
O4–H4B···O3	2.47	2.868(5)	108.0
O5–H5B···O4^{ii}	2.06	2.809(6)	164.0
O6–H6A···O5	1.76	2.759(5)	175.0
Between water network and N-azide or N-PTA			
O1–H1B···N3^{iii}	2.07(4)	2.914(7)	173(6)
O2–H2B···N22	2.21	2.991(6)	165.0
O3–H3A···N11^{iv}	2.02	2.873(6)	170.0
O4–H4A···N21^{v}	2.04	2.871(5)	173.0
Other H-contacts			
C12–H12B···N6^{vi}	2.51	3.305(7)	138.00
C14–H14A···O5^{vii}	2.59	3.394(7)	138.00
C15–H15B···N6^{viii}	2.61	3.586(8)	168.00
C16–H16B···N4^{iii}	2.57	3.521(8)	161.00
C16–H16B···N5^{iii}	2.45	3.398(7)	161.00

[a] Symmetry codes: (i) $-x$, y, $\frac{1}{2} - z$; (ii) x, $1+ y$, z; (iii) $\frac{1}{2} - x$, $3/2 - y$, $-z$; (iv) $\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$; (v) x, $-1 + y$, z; (vi) $\frac{1}{2} - x$, $5/2 - y$, $-z$; (vii) $\frac{1}{2} - x$, $1/2 + y$, $\frac{1}{2} - z$; (viii) x, $2 - y$, $\frac{1}{2} + z$.



Scheme 1 Syntheses of platinum(II) complexes with PTA and Me-PTA.

Results and discussion

Syntheses and characterization of the azide-PTA complexes 1–3

The reaction of stoichiometric quantities of PTA and *cis*-$[Pt(N_3)_2(PPh_3)_2]$ (Pt : PTA = 1 : 2) in CH_2Cl_2 at room temperature leads to the precipitation of *cis*-$[Pt(N_3)_2(PTA)_2]$ (**1**) as an off-white microcrystalline solid in 83% yield (Scheme 1). The analogous compound with *N*-methylated PTA *cis*-$[Pt(N_3)_2(Me\text{-}PTA)_2]I_2$ (**2**) was obtained as a pale-yellow solid (80% yield) from the reaction with [Me-PTA]I, under similar conditions (Scheme 1). However, treatment of *cis*-$[Pt(N_3)_2(PPh_3)_2]$ with an excess of PTA (Pt : PTA = 1 : 3), in the same solvent, affords the penta-coordinate tris(PTA) complex $[Pt(N_3)_2(PTA)_3]$ (**3**) in 58% isolated yield, which is soluble in CH_2Cl_2.

Complexes **1–3** are air-stable as solids and in water solution. Although they are readily soluble in H_2O and in other polar solvents, such as Me_2SO, NCMe and $Me_2C(O)NH_2$, they are less soluble in MeOH and insoluble in Et_2O and in apolar solvents such as C_6H_{14} and CCl_4. Complex **3**, in contrast to **1** and **2**, is also soluble in solvents like $CHCl_3$, CH_2Cl_2 and EtOH with medium polarity.

The complexes have been characterized by elemental analysis, FAB-MS, IR, ^1H and ^{31}P NMR spectroscopies. The FAB-MS spectra of **1** and **3** show the expected isotopic pattern for the respective molecular ion $[M]^+$, and for all the compounds the peaks corresponding to the stepwise fragmentation by loss of the azide ligands, $[M\text{-}(N_3)]^+$ and $[M\text{-}2(N_3)]^+$, are also detected. The IR spectra of **1–3** exhibit the typical azide band in the range 2060–2033 cm^{-1}. The ^1H NMR spectra of the PTA complexes **1** and **3** at 298 K show two types of methylene protons. One of them, P–CH_2-N, occurs as a broad singlet at 4.23 and 4.24 ppm for **1** and **3** respectively. The second type, N–CH_2-N, displays an AB spin system centred at 4.53 and 4.28 ppm for **1** and **3**respectively (J_{AB} = 13 Hz for both compounds), assigned to the N–CH_{ax}-N and the N–CH_{eq}-N protons.[26] The Me-PTA compound *cis*-$[Pt(N_3)_2(Me\text{-}PTA)_2]I_2$ **2** displays in the ^1H NMR spectrum the expected[10b] four types of methylene protons: NCH_2N^+, NCH_2N, PCH_2N (as AB spin systems centred at 5.10, 4.36 and 4.42 ppm respectively) and PCH_2N^+ (singlet at 4.89 ppm).

The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** show singlets with platinum satellites, at −59.1 and −47.2 ppm. The values of the $J_{Pt\text{-}P}$ coupling (3139 or 3153 Hz respectively) clearly show the *cis* phosphine configuration.[16b,27] The penta-coordinate complex $[Pt(N_3)_2(PTA)_3]$ (**3**) exhibits a fluxional behaviour in solution as shown by variable temperature $^{31}P\{^1H\}$ NMR (in $CDCl_3$). Although at 298 K no resonances could be identified, cooling the solution until 213 K (Fig. 2) results in the appearance of a clear pattern consisting of one doublet and one triplet ($^2J_{PP}$ = 23.5 Hz, intensities of 2 : 1) at −57.6 and −51.6 ppm, respectively, with the corresponding platinum satellite ($J_{Pt\text{-}P}$ = 2187 and 3304 Hz, respectively). They are assigned to the two PTA ligands in

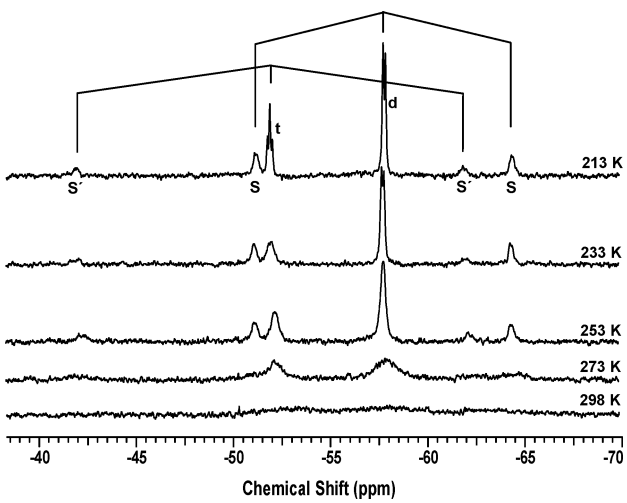


Fig. 2 Variable temperature $^{31}P\{^1H\}$ NMR spectra of **3** in $CDCl_3$ (d, doublet; t, triplet). ^{195}Pt satellites are denoted by **S** and **S′**.

mutually *trans* position and to the unique PTA, either in a square pyramidal or trigonal bipyramidal geometry, or a distorted form. The tris(PTA) complexes $[Pt(N_3)(PTA)_3]^+$[18] and $[PtI_2(PTA)_3]$[19] (the latter also penta-coordinate as **3**), in D_2O and at room temperature, also exhibit broad overlapping ^{31}P NMR peaks, but a coupling system similar to that of the low-temperature limit spectrum of **3** is observed[18] at room temperature for $[Pt(Br)(PTA)_3]^+$ in D_2O.

Solution (in nitromethane) conductivity measurements of **1–3** (see experimental) confirm the expected non-electrolyte nature of **1** and **3** and the 1 : 2 electrolyte behaviour of **2** (the molar conductivity falls in the typical range for such an electrolyte[28]). Moreover, treatment of an aqueous solution of **2** with $AgNO_3$ in water readily leads to the formation of a AgI precipitate in the amount corresponding to the presence of the two iodide counter-ions.

X-Ray crystal structure of 1†

Compound **1** crystallizes in the monoclinic space group *C*2/*c* (Fig. 3), the moiety formula including 2 molecules of the metal–organic moiety and 11 molecules of water. Crystal and refinement data, selected interatomic distances and angles are given in Tables 1 and 2. The platinum atom is coordinated in a slightly distorted square planar geometry with the phosphines and the end-on azide ligands in the *cis* orientation. The azide ligands are almost linear [N1–N2–N3 and N4–N5–N6 angles of 174.2(6) and 174.6(6)° respectively], with corresponding Pt1–N1–N2 and Pt1–N4–N5 angles of 121.7(4) and 122.1(4)°. The azide N–N bonds adjacent to the azide Pt–N bond (N1–N2 and N4–N5, av. 1.209 Å) are significantly longer than the terminal azide N–N bond (N2–N3 and N5–N6, av. 1.156 Å), which is common for coordinated azides.[29] The Pt–P bond lengths (av. 2.227 Å) are similar to those in *cis*-$[PtX_2(PTA)_2]$ (X = Cl, Br and I).[16b]

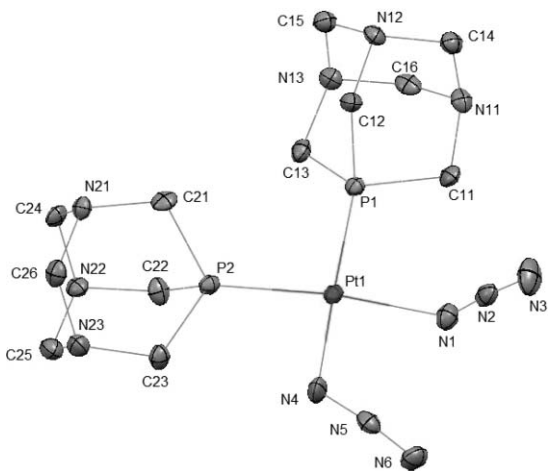


Fig. 3 Thermal ellipsoid (50% probability) plot of compound **1** with atomic numbering scheme. Hydrogens atoms and water molecules were omitted for clarity.

The single-crystal X-ray examination of compound **1** shows that it forms, in the solid state, 3D hydrogen bonded metal–organic frameworks with intercalated crystallization water molecules, which outline extensive hydrogen bonding with the terminal N3 azide atom and the N11, N21 and N22 of the PTA ligands (Table 2 and Fig. 4). Additional contact interactions involving the N4, N5 and N6 atoms of one of the azides as well as O5 water oxygen with PTA methylene hydrogens, help to stabilize the structure. Moreover, the intercalated crystallization water molecules are associated to form symmetry-generated infinite water clusters composed of alternatively linked cyclic decamers and pentamers (Fig. 5). The average O···O contact of *ca.* 2.79 Å is similar to that found in the structure of ice,[30,31] and to those reported[32–41] for other hosted water clusters.

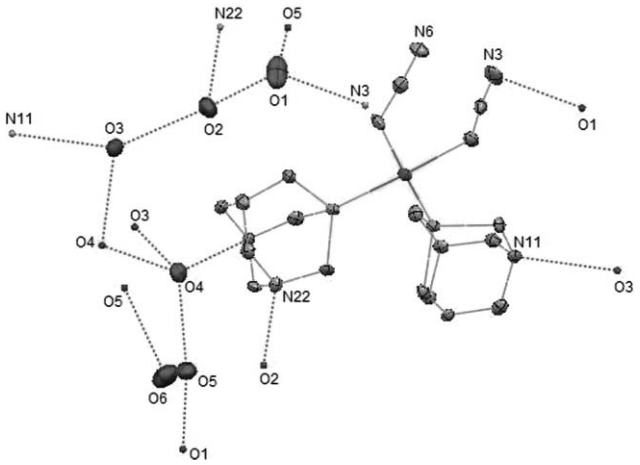


Fig. 4 Hydrogen bonding network (dashed lines) and atom labeling scheme (hydrogen atoms are omitted for clarity) showing the interactions involving all water molecules (O6 is in a special position with 1/2 of site occupation), the terminal *N*-azide and some PTA-N atoms, which provides the formation of a 3D assembly.

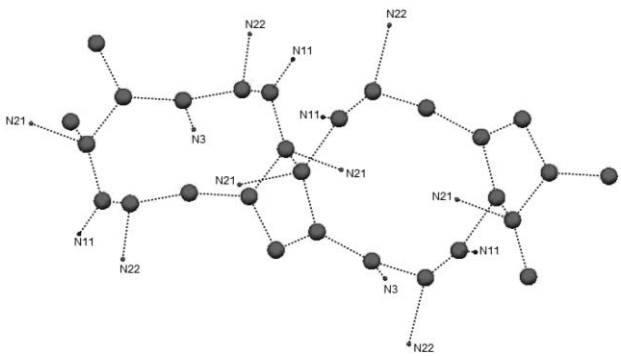


Fig. 5 Perspective representation (arbitrary view) of the extended cyclic crystallization water clusters hosted in the matrix of **1**, showing alternate cyclic decamers and pentamers. Hydrogens were omitted for clarity.

The crystal packing diagrams in Fig. 6 show layers of water clusters trapped by two metal–organic chains. In Fig. 6b, the vertical separation between neighbouring $[Pt(N_3)_2(PTA)_2]$ layers, *i.e.* between the planes (010) and (020), is of 4.642 Å (half the *b* axis) and the horizontal separation between water layers, *i.e.*, between the planes (100) and (200), is of 13.251 Å (half the *a* axis).

Syntheses and characterization of the tetrazolato-PTA complexes 4–6

The bis(tetrazolato) complexes *trans*-$[Pt(N_4CR)_2(PTA)_2]$ [R = Ph (**4**), 4-ClC_6H_4 (**5**) or 3-NC_5H_4 (**6**)] were obtained by reaction of *cis*-$[Pt(N_3)_2(PTA)_2]$ **1** with the appropriate organonitrile NCR, which

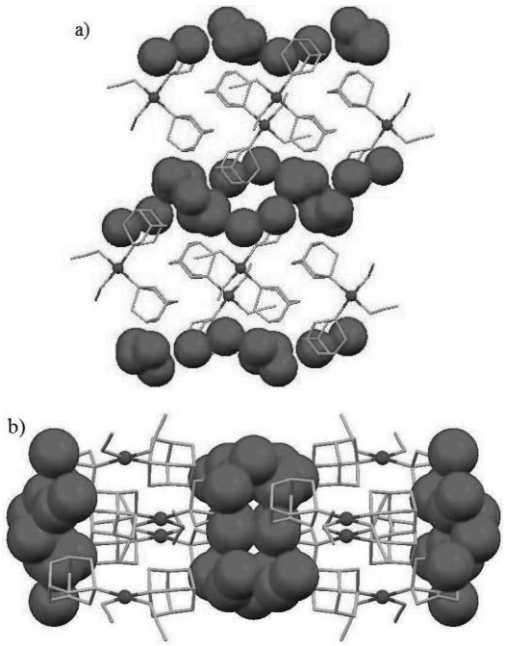
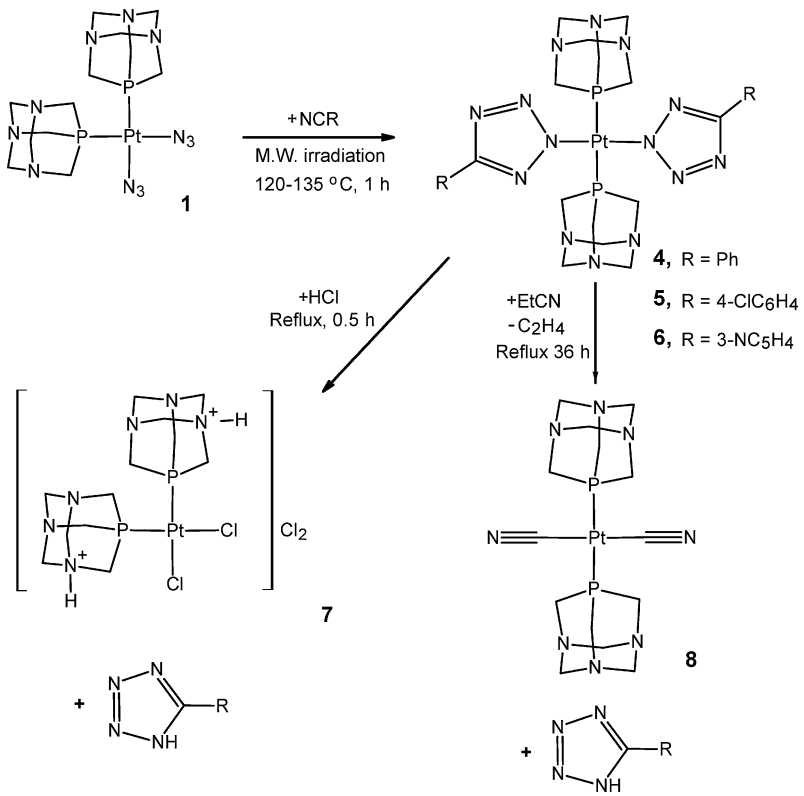


Fig. 6 Fragment of the crystal packing diagram of **1** showing two parallel metal–organic frameworks of $[Pt(N_3)_2(PTA)_2]$ with three intercalated layers of water water clusters represented by a space-filling model viewed along the crystallographic (a) *b* and (b) *c* axes.

is accelerated by microwave irradiation (typically at 120–135 °C, for 1 h). They were isolated in moderate yields (*ca.* 60–65%) as off-white powders (Scheme 2) and are stable in the solid state and in solution under air. They are readily soluble in middle polar solvents, such as $CHCl_3$, CH_2Cl_2, sparingly soluble in polar ones such as MeOH, MeCN, Me_2SO and $Me_2C(O)NH_2$, and insoluble in low polar and apolar solvents like Et_2O, C_6H_6 and CCl_4. **5** and **6** are also sparingly soluble in H_2O. Complexes **4–6** have been characterized by elemental analysis, FAB-MS, IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. Their IR spectra in KBr display a strong band within the 1615–1630 cm^{-1} range due to the tetrazole ring, in agreement with the literature[42] The FAB-MS spectra show the isotopic pattern for the corresponding complex molecular ion $[M]^+$ and peaks resulting from the fragmentations by loss of one tetrazole, *i.e.* due to $[M\text{-}(N_4CR)]^+$. Their ^1H NMR spectra, in $CDCl_3$ at ambient temperature, show two patterns of methylene protons for the coordinated PTA, similarly to complexes **1–3**, and the phenyl ring pattern for **4** and **5**, and that of the pyridyl group for **6**. In contrast to the PPh_3 complex *trans*-$[Pt(N_4CR)_2(PPh_3)_2]$[7], the $^{31}P\{^1H\}$ NMR spectra of **4–6** exhibit singlets with platinum satellites at δ −56.2, −56.3 and −56.2, with $J_{Pt\text{-}P}$ of 2497, 2491 and 2479 Hz, respectively. These coupling values clearly show the *trans* configuration of the phosphines[27], and the singlet resonance indicates the existence of only one type of *N*-coordination of the tetrazoles (the sterically favourable N^2 mode, as established in the solid state by X-ray diffraction, see below). The *cis*-to-*trans* conversion of *cis*-$[Pt(N_3)_2(PTA)_2]$ (**1**) into *trans*-$[Pt(N_4CR)_2(PTA)_2]$ (**4–6**) is similar to that of *cis*-$[Pt(N_3)_2(PPh_3)_2]$[7] into *trans*-$[Pt(N_4CR)_2(PPh_3)_2]$. Thermal isomerizations of *cis*-$[Pt(Cl)_2(RCN)_2]$ into *trans*-$[Pt(Cl)_2(RCN)_2]$ have been reported previously[43,44] and indicate that the *trans* isomer is thermodynamically more favoured.



Scheme 2 Syntheses of the bis(tetrazolato) complexes *trans*-$[Pt(N_4CR)_2(PTA)_2]$ (**4–6**) and the corresponding 5-substitued-1H-tetrazoles HN_4CR.

X-Ray crystal structure of 4†

Crystals of compound **4** suitable for X-ray analysis were obtained from slow evaporation of a $CHCl_3$–toluene solution at room temperature. A view of the complex is shown in Fig. 7, crystal data and selected bond lengths and angles are given in Tables 1 and 3 respectively. The platinum center is tetracoordinated in a slightly distorted planar geometry with both the phosphine and the tetrazolate ligands in mutually *trans* positions. The tetrazolates are coordinated to the metal centre by the N^2-nitrogen atom of the ring. Each pyridyltetrazolato ligand is roughly planar but their planes are twisted as indicated by the non-equivalence of the torsion angles P1–Pt1–N5–N8 [27.1(12)°] and P1–Pt1–N1–N4 [95.0(11)°]. The structure of **4** is similar to that previously described for the related platinum complex with PPh_3, *i.e. trans*-$[Pt(N_4CPh)_2(PPh_3)_2]$.[7] While the Pt–N distances in **4** are comparable to those in **1**, the Pt–P bond distances in the former are longer than those in the latter (Table 1) as a result of the stronger *trans* influence of the phosphorus moiety (in **4**) as compared to azide (in **1**).

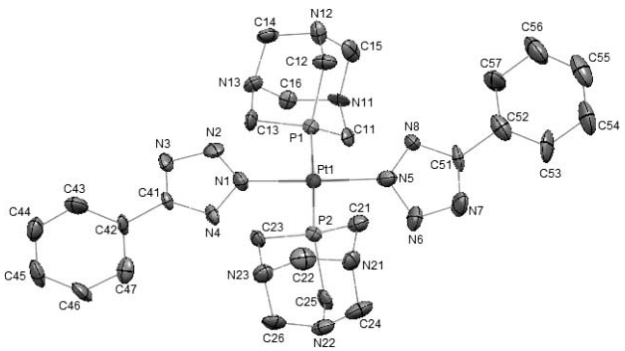


Fig. 7 Molecular structure of *trans*-$[Pt(N_4CPh)_2(PTA)_2]$ **4** with atomic numbering scheme (hydrogens were omitted for clarity). Displacement ellipsoids are drawn at the 50% probability level.

Interestingly, the exposed sides of the platinum ion (perpendicular to the plane defined by the coordinated P and N atoms) form two short contacts to H atoms (H12A and H22A) of methylene groups of PTA in neighbouring molecules (Fig. 8) with the C12 ··· Pt and C22 ··· Pt bond distances being 3.532(14) and 3.519(13) Å. These distances are short, as compared with the sum of the van der Waals radii, 4.0 Å, of carbon and platinum. Such intermolecular pseudo-agostic (IPA)[45] interactions appear to play a role in the packing of the structure.

Table 3 Crystal data and structure refinement details for **1** and **4**

Empirical formula	$C_{24}H_{70}N_{24}O_{11}P_4Pt_2$	$C_{26}H_{34}N_{14}P_2Pt$
Formula weight	1385.08	799.69
Crystal system, space group	Monoclinic, $C2/c$	Triclinic, $P\bar{1}$
a/Å	27.079(7)	6.176(2)
b/Å	9.284(3)	16.211(6)
c/Å	18.982(5)	17.019(6)
α/°	90	95.176(19)
β/°	101.845(16)	92.28(2)
γ/°	90	94.15(2)
Volume/Å^3	4670(2)	1690.8(10)
Z, calculated density ρ_{calc}/Mg m^{-3}	4, 1.970	2, 1.571
F(000)	2744	792
Reflections collected/unique	14 147/4761 [R(int) = 0.0477]	14 928/6209 [R(int) = 0.1264]
Data/restraints/parameters	4761/1/297	6209/0/388
Goodness-of-fit on F^2	0.982	0.976
Final $R1$,[a] w$R2$[b] ($I \geq 2\sigma$)	$R1$ = 0.0311, w$R2$ = 0.0629	$R1$ = 0.0787, w$R2$ = 0.1723

[a] $R1 = \sum\|F_o\| - |F_c\|/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

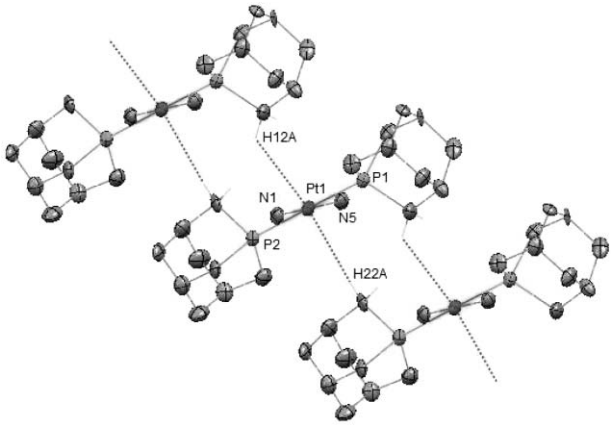


Fig. 8 Fragment of the crystal packing diagram (arbitrary view) of **4** showing the short $CH_2 \cdots Pt$ contacts: Pt1 ··· H12A 2.850 Å and Pt1 ··· H22A 2.920 Å. The tetrazol ligands and hydrogen atoms were omitted for clarity.

Liberation and characterization of the 5-R-1H-tetrazoles HNN_3CR (R = Ph, 4-ClC_6H_4 or 3-NC_5H_4)

Liberation of the ligated tetrazoles from the coordination sphere of the complexes **4–6** was an important aim of the current study, and this was achieved by two different methods, one by treatment with aqueous HCl and the other by reaction with propionitrile. The former method is more effective, simpler and also advantageous in terms of providing an easier separation of the tetrazole products. It involves simple refluxing, for 0.5 h, a suspension of the appropriate tetrazolato *trans*-$[Pt(N_4CR)_2(PTA)_2]$ complex in aqueous 0.1 M HCl, leading to spontaneous precipitation in high yield (*ca.* 80%) of the corresponding 5-R-1H-tetrazole. This product is not water soluble, in contrast with the chloro-complex *cis*-$[Pt(Cl)_2(PTA\text{-}H)_2]Cl_2$ **7** that is also formed (Scheme 2) which bears protonated PTA and remains in aqueous medium. Its $^{31}P\{^1H\}$ NMR spectrum shows one singlet (δ –47.9) with platinum satellites ($J_{Pt\text{-}P}$ 3480 Hz) indicative[16b,27] of the *cis* phosphines configuration. These data are comparable to those reported[46] for *cis*-$[Pt(Cl)_2(PTA)_2]$, although the ^{31}P resonance of **7** is at a lower field than that (δ –50.4) of the latter complex in view of the effect of the PTA protonation, as has been previously reported[26a] for $[ReCl(N_2)(PTA\text{-}H)_n(PTA)_{4-n}]^{n+}$ (n = 1–4).

The second method for liberating the tetrazolato ligands from complexes **4–6** involves refluxing a solution of any of these complexes in propionitrile for 36 h. Further working up (concentration and addition of diethyl ether) leads to the precipitation of the dicyano complex *trans*-$[Pt(CN)_2(PTA)_2]$ **8** (Scheme 2), the 5-R-1H-tetrazoles being isolated only after evaporation of the mother liquor to dryness. The reaction is believed to proceed *via* oxidative addition of propionitrile with NC–C bond cleavage followed by reductive elimination and evolution of ethylene, as

we have previously observed[7] for the related reactions of *trans*-$[Pt(N_4CR)_2(PPh_3)_2]$ with $N{\equiv}CC_2H_5$.

The crystal structure of *trans*-$[Pt(CN)_2(PTA)_2]$ **8** was previously determined[47] but no spectroscopic data were reported. Hence, we have now additionally characterized this compound by IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. It exhibits in the ^1H NMR spectrum, in DMSO-d_6, singlets at δ 4.62 and 4.43 assigned to the two types of methylene protons, *i.e.* NCH_2N and PCH_2N respectively. The $^{31}P\{^1H\}$ NMR spectrum displays the expected singlet at δ –64.5 with the platinum satellites ($J_{Pt\text{-}P}$ = 2050 Hz, indicative[27] of the *trans* phosphine configuration). The $^{13}C\{^1H\}$ NMR (singlet at δ 126.9) and IR (strong band at 2127 cm^{-1}) data confirm the presence of the cyano ligands in **8**.

The liberated 5-R-1H-tetrazoles (R = Ph, 4-ClC_6H_4 and 3-NC_5H_4) were characterized by IR, ^1H and $^{13}C\{^1H\}$ spectroscopies and by ESI-MS. In particular ^{13}C NMR resonance of the C=N tetrazole ring carbon atom is observed at a higher field (148–156 ppm) than that of the corresponding complex **4–6** (*ca.* 164 ppm).

Although the tetrazolates, in the Pt complexes, are coordinated by the N^2-nitrogen atom of the (N_4C) ring, the liberated tetrazoles are expected to be in the 1H-tautomeric form (with the H atom at N^1). This is the privileged one in the solid state,[48] although in solution a tautomeric equilibrium can occur, being strongly dependednt on the experimental conditions.[48,49] The N^1–N^2 linkage isomerization of tetrazolato ligands is also possible, as known for Pt[7,50] and Co[51] metal centres.

Conclusions

We have found a simple route for new water-soluble azido-platinum(II) complexes based on reaction of *cis*-$[Pt(N_3)_2(PPh_3)_2]$ with hydrosoluble PTA or [PTA-Me]I at room temperature. As shown for one of the complexes, *cis*-$[Pt(N_3)_2(PTA)_2]$, these azido-compounds can be applied as starting materials for the platinum mediated synthesis of 5-substituted tetrazoles upon [2 + 3] cycloadditions with organonitriles NCR to give bis(tetrazolato) complexes *trans*-$[Pt(N_4CR)_2(PTA)_2]$ from which the tetrazoles can be not only conveniently liberated but also conveniently isolated in a pure form on account, on one hand, of the high water solubility of the concomitantly formed PTA-platinum complex and, on the other hand, of the water insolubility of the tetrazole which spontaneously precipitates out of the solution. In this way, the 5-substituted tetrazoles are obtained and isolated as solids (in a high yield) in a easy single-pot process upon simple treatment of the respective tetrazolato complexes with aqueous diluted HCl, the other metal containing product, *cis*-$[Pt(Cl)_2(PTA\text{-}H)_2]^{2+}$, remaining in the mother aqueous solution.

This type of approach for metal- mediated synthesis and easy isolation of water-insoluble organonitrogen compounds, based on the use of hydrosoluble PTA complexes, is expected to be applicable to many other cases and its extension to different reactions is under way in our laboratory.

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References

1 (*a*) V. Y. Kukushkin and A. J. L. Pombeiro, *Chem. Rev.*, 2002, **102**, 1771; (*b*) H.-W. Frühauf, *Chem. Rev.*, 1997, **97**, 523; (*c*) R. A. Michelin, M. Mozzon and R. Bertani, *Coord. Chem.Rev.*, 1996, **147**, 299; (*d*) R. J. Herr, *Bioorg. Med. Chem.*, 2002, **10**, 3379; (*e*) L. Myznikov, A. Hrabalek and G. Koldobskii, *Chem. Heterocycl. Comp.*, 2007, **43**, 1; (*f*) K. V. Gothelf and K. A. Jφrgensen, *Chem. Rev.*, 1998, **98**, 863.
2 (*a*) S. Wee, M. J. Grannas, W. D. McFadyen and R. A. J. O'Hair, *Aust. J. Chem.*, 2001, **54**, 245; (*b*) P. Paul and K. Nag, *Inorg. Chem.*, 1987, **26**, 2969; (*c*) Y.-J. Kim, J.-T. Han, S. Kang, W. S. Han and S. W. Lee, *Dalton Trans.*, 2003, 3357; (*d*) Y.-J. Kim, Y.-S. Kwak, Y.-S. Joo and S. W. Lee, *J. Chem. Soc. Dalton Trans.*, 2002, 144.
3 W. P. Fehlhammer, T. Kemmerich and W. Beck, *Chem. Ber.*, 1983, **116**, 2691.
4 (*a*) J. V. Duncia, M. E. Pierce and J. B. Santella III, *J. Org. Chem.*, 1991, **56**, 2395; (*b*) B. E. Huff and M. A. Staszak, *Tetrahedron Lett.*, 1993, **34**, 8011; (*c*) S. J. Wittenberger and B. G. Donner, *J. Org. Chem.*, 1993, **58**, 4139; (*d*) K. Koguro, T. Oga, S. Mitsui and R. Orita, *Synthesis*, 1998, 910; (*e*) D. P. Curran, S. Hadida and S.-Y. Kim, *Tetrahedron*, 1999, **55**, 8997.
5 (*a*) Z. P. Demko and K. B. Sharpless, *J. Org. Chem.*, 2001, **66**, 7945; (*b*) F. Himo, Z. P. Demko, L. Noodleman and K. B. Sharpless, *J. Am. Chem. Soc.*, 2002, **124**, 12210; (*c*) F. Himo, Z. P. Demko, L. Noodleman and K. B. Sharpless, *J. Am. Chem. Soc.*, 2003, **125**, 9983.
6 D. Amantini, R. Beleggia, F. Fringuelli, F. Pizzo and L. Vaccaro, *J. Org. Chem.*, 2004, **69**, 2896.
7 S. Mukhopadhyay, J. Lasri, M. A. J. Charmier, M. F. C. Guedes, da Silva and A. J. L. Pombeiro, *Dalton Trans.*, 2007, 5297.
8 A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza and M. Peruzzini, *Coord. Chem. Rev.*, 2004, **248**, 955.
9 (*a*) S. Bolaño, L. Gonsalvia, F. Zanobinia, F. Vizza, V. Bertolasi, A. Romerosa and M. Peruzzini, *J. Mol. Cat. A*, 2004, **224**, 61; (*b*) F. Joó, *Aqueous Organometallic Catalysis*, Kluwer Academic Publishers, Dordrecht, 2001; *Aqueous Phase Organometallic Catalysis*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 1998; *Aqueous Organometallic Chemistry and Catalysis*, ed. I. T. Horvath and F. Joó, NATO ASI Series 3/5, Kluwer Academic Publishers, Dordrecht, 1995.
10 (*a*) P. Smoleński, F. P. Pruchnik, Z. Ciunik and T. Lis, *Inorg. Chem.*, 2003, **42**, 3318; (*b*) F. P. Pruchnik and P. Smoleński, *Appl. Organomet. Chem.*, 1999, **13**, 829; (*c*) F. P. Pruchnik, P. Smoleński and K. Wajda-Hermanowicz, *J. Organomet. Chem.*, 1998, **570**, 63; (*d*) F. P. Pruchnik, P. Smoleński, E. Gałdecka and Z. Gałdecki, *New J. Chem.*, 1998, 1395; (*e*) F. P. Pruchnik, P. Smoleński, E. Gałdecka and Z. Gałdecki, *Inorg. Chim. Acta*, 1999, **293**, 110; (*f*) F. P. Pruchnik, P. Smoleński and I. Raksa, *Polish J. Chem.*, 1995, **69**, 5.
11 (*a*) A. Dorcier, W. H. Ang, S. Bolaño, L. Gonsalvi, L. Juillerat-Jeannerat, G. Laurenczy and M. Peruzzini, *Organometallics*, 2006, **25**, 4090; (*b*) A. D. Phillips, F. Zanobini, P. J. Dyson, C. Scolaro, T. J. Geldbach, S. Rochat, A. Dorcier, C. Gossens, A. Bergamo, M. Cocchietto, I. Tavernelli, G. Sava, U. Rothlisberger and P. J. Dyson, *Organometallics*, 2006, **25**, 756.
12 C. Scolaro, A. Bergamo, L. Brescacin, R. Delfino, M. Cocchietto, G. Laurenczy, T. J. Geldbach, G. Sava and P. J. Dyson, *J. Med. Chem.*, 2005, **12**, 4161.
13 B. Serli, E. Zangrando, T. Gianferrara, C. Scolaro, P. J. Dyson, A. Bergamo and E. Alessio, *Eur. J. Inorg. Chem.*, 2005, 3423.
14 F. Mohr, S. Sanz, E. R. T. Tiekink and M. Laguna, *Organometallics*, 2006, **25**, 3084.
15 F. Mohr, E. Cerrada and M. Laguna, *Organometallics*, 2006, **25**, 644.
16 (*a*) D. A. Krogstad, J. Cho, A. J. DeBoer, J. A. Klitzke, W. R. Sanow, H. A. Williams and J. A. Halfen, *Inorg. Chim. Acta*, 2006, **359**, 136; (*b*) D. A. Krogstad, S. B. Owens, J. A. Halfen and V. G. Young, Jr., *Inorg. Chem. Comm.*, 2005, **8**, 65.
17 P. Bergamini, V. Bertolasi, L. Marvelli, A. Canella, R. Gavioli, N. Mantovani, S. Manãs and A. Romerosa, *Inorg. Chem.*, 2007, **46**, 4267.
18 Z. A. Sam, A. Roodt and S. Otto, *J. Coord. Chem.*, 2006, **59**, 1025.
19 S. Otto and A. Roodt, *Inorg. Chem. Comm.*, 2001, **4**, 49.
20 (*a*) D. J. Daigle, A. B. Pepperman, Jr. and S. L. Vail, *J. Heterocycl. Chem.*, 1974, **11**, 407; (*b*) D. J. Daigle, *Inorg. Synth.*, 1998, **32**, 40.
21 J. Erbe and W. Beck, *Chem. Ber.*, 1983, **116**, 3867.
22 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467.
23 G. M. Sheldrick, *SHELXL-97*, University of Gottingen, Germany, 1997.
24 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

25 A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **49**, C34.
26 (*a*) P. Smoleński and A. J. L. Pombeiro, *Dalton Trans.*, 2008, 87; (*b*) A. M. Kirillov, P. Smoleński, M. F. C. Guedes, da Silva and A. J. L. Pombeiro, *Eur. J. Inorg. Chem.*, 2007, 2686.
27 (*a*) M. F. C. Guedes, da Silva, E. M. P. R. P. Branco, Y. Wang, J. J. R. Fraústo, da Silva, A. J. L. Pombeiro, R. Bertani, R. A. Michelin, M. Mozzon, F. Benetollo and G. Bombieri, *J. Organomet. Chem.*, 1995, **490**, 89; (*b*) R. A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo, M. F. C. Guedes, da Silva and A. J. L. Pombeiro, *Organometallics*, 1993, **12**, 2372.
28 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
29 (*a*) P. Müller, B. Schröder, J. A. Parkinson, N. A. Kratochwil, R. A. Coxall, A. Parkin, S. Parsons and P. J. Sadler, *Angew. Chem. Int. Ed.*, 2003, **42**, 335; (*b*) T. Suzuki, *Acta Cryst.*, 2005, **E61**, m488-m490.
30 O. Ermer and J. Neudorfl, *Chem. Eur. J.*, 2001, **7**, 4961.
31 U. Mukhopadhyay and I. Bernal, *Cryst. Growth Des.*, 2006, **6**, 363.
32 Y. Y. Karabach, A. M. Kirillov, M. F. C. Guedes, da Silva, M. N. Kopylovich and A. J. L. Pombeiro, *Cryst. Growth Des.*, 2006, **6**, 2200.
33 M. Mascal, L. Infantes and J. Chisholm, *Angew. Chem. Int. Ed.*, 2006, **45**, 32.
34 L. Infantes, J. Chisholm and S. Motherwell, *Cryst. Eng. Comm.*, 2003, **5**, 480.
35 L. Infantes and S. Motherwell, *Cryst. Eng. Comm.*, 2002, **4**, 454.
36 Y. Li, L. Jiang, X.-L. Feng and T.-B. Lu, *Cryst. Growth Des.*, 2006, **6**, 1074.
37 A. Michaelides, S. Skoulika, E. G. Bakalbassis and J. Mrozinski, *Cryst. Growth Des.*, 2003, **3**, 487.
38 R. D. Bergougnant, A. Y. Robin and K. M. Fromm, *Cryst. Growth Des.*, 2005, **5**, 1691.
39 M. Yoshizawa, T. Kusukawa, M. Kawano, T. Ohhara, I. Tanaka, K. Kurihara, N. Niimura and M. Fujita, *J. Am. Chem. Soc.*, 2005, **127**, 2798.
40 L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 2000, 859.
41 L. J. Barbour, G. W. Orr and J. L. Atwood, *Nature*, 1998, **393**, 671.
42 P. Lin, W. Clegg, R. W. Harrington and R. A. Henderson, *Dalton Trans.*, 2005, 2388.
43 P. Svensson, K. Lovqvist, V. Y. Kukushkin and Å. Oskarsson, *Acta Chem. Scand.*, 1995, **49**, 72.
44 T. Uchiyama, Y. Toshiyasu, Y. Nakamura, T. Miwa and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 181.
45 D. Braga, F. Grepioni and G. R. Desiraju, *Chem Rev.*, 1998, **98**, 1375.
46 (*a*) S. Otto, A. Roodt and W. Purcell, *Inorg. Chem. Comm.*, 1998, **1**, 415; (*b*) D. J. Darensbourg, T. J. Decuir, N. W. Stafford, J. B. Robertson, J. D. Draper, J. H. Reibenspies, A. Kathó and F. Joó, *Inorg. Chem.*, 1997, **36**, 4218.
47 Z. Assefa, B. G. McBurnett, R. J. Staples and J. P. Fackler, *Acta Cryst. C*, 1995, **51**, 1742.
48 M. W. Wong, R. Leung-Toung and C. Wentrup, *J. Am. Chem. Soc.*, 1993, **115**, 2465.
49 D. Kurz and J. Reinhold, *THEOCHEM*, 1999, **492**, 187.
50 A. V. Khripun, V. Y. Kukushkin, G. I. Koldobskii and M. Haukka, *Inorg. Chem. Comm.*, 2007, **10**, 50.
51 W. G. Jackson and S. Cortez, *Inorg. Chem.*, 1994, **33**, 1921.