

A Silver(I) Coordination Polymer Containing Tridentate *N*- and *P*-Coordinating 1,3,5-Triaza-7-phosphaadamantane (PTA) Ligands

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Dedicated to Prof. Victor Riera on the occasion of his retirement for his contribution to inorganic chemistry

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A silver(I) coordination polymer containing 1,3,5-triaza-7-phosphaadamantane (PTA) in an unprecedented bridging, tridentate *P,N,N'*-coordination mode is formed by the reaction of PTA with AgNO₃ in water.

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The synthesis of the air-stable, water-soluble phosphane ligand 1,3,5-triaza-7-phosphaadamantane (PTA) was first reported in 1974^[1] but only recently has this phosphane been used as a ligand in a variety of inorganic and organometallic compounds.^[2] An important driving force for the sudden interest in this ligand has been due to further developments in “green chemistry” and the need for inorganic/organometallic compounds that are soluble and stable in aqueous media.^[3,4] One strategy to solubilise metal compounds is by the coordination of water-soluble ligands to a metal centre, which then may impart water solubility to the entire complex. In almost all of the known PTA metal complexes, the phosphane acts as a *P*-donor ligand (Figure 1, A). Very recently, the first examples of transition metal compounds that contain *N*-coordinated PTA (Figure 1, B) have been observed in manganese complexes [MnX₂(PTA)₂(H₂O)₂] (X = Cl, Br).^[5] In 2005, the organometallic Ru/Ag coordination polymers [CpRu(L)(μ-*P,N*-PTA)₂-AgCl₂]_n (L = dmsO, H₂O) were reported, which constitute the first, and so far only, examples of a PTA complex in which the ligand adopts a bridging *N,P*-coordination mode (Figure 1, C).^[6]

In the past, we have utilised silver(I) phosphane salts of the type [AgX(P)] (P = tertiary phosphane; X = OTf, ClO₄, NO₃) as phosphane transfer reagents in the preparation of gold(II) complexes by metathesis reactions.^[7] Recently, we reported the synthesis and characterisation of a series of

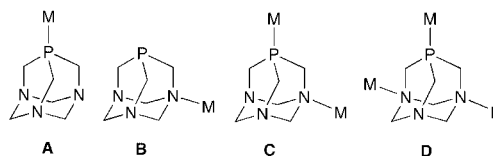


Figure 1. Observed coordination modes of PTA.

water-soluble and water-stable gold complexes, which includes a gold(II) PTA derivative that was prepared with [Ag(OTf)(PTA)].^[8,9] During our studies of various [AgX(PTA)] derivatives, we isolated and structurally characterised the nitrate derivative [Ag(PTA)(H₂O)]NO₃. X-ray quality crystals of [Ag(PTA)(H₂O)]NO₃^[10] were formed when aqueous solutions containing equimolar amounts of PTA and AgNO₃ were mixed. This compound is the first example of a complex that contains PTA in a triply bridging *P,N,N'*-coordination mode (Figure 1, D). The basic unit of this complex consists of a molecule of *P*-coordinated PTA and water coordinated to the silver atom (Figure 2).

These monomers are then arranged such that two of the PTA nitrogen atoms, N-2 and N-3, coordinate to other silver atoms, i.e. each silver atom is connected to one phosphorus atom, P-1, and two nitrogen atoms, N-2 and N-3, from three different PTA molecules in a T-shaped arrangement. The coordinated water molecule completes the distorted tetrahedral coordination geometry about the silver atom. The network structure of the complex can be described as a polymeric net that contains hexagonal units (Figure 3).

In the crystal, these polymeric nets are stacked above each other, and the resulting channels are occupied by the nitrate anions (Figure 4).

In this complex, the PTA ligand behaves very similarly to its all-nitrogen analogue hexamethylenetetramine

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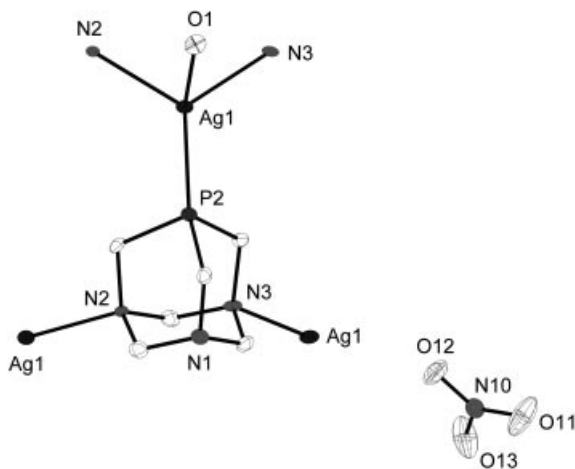


Figure 2. Structure of $[\text{Ag}(\text{PTA})(\text{H}_2\text{O})]\text{NO}_3$ which shows the atom-labelling scheme. Displacement ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity.

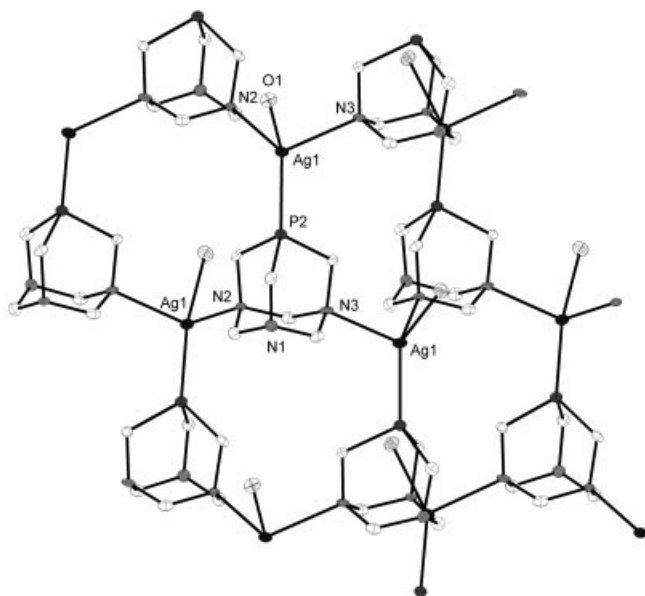


Figure 3. Polymeric net structure of $[\text{Ag}(\text{PTA})(\text{H}_2\text{O})]\text{NO}_3$ which illustrates the P,N,N' -coordination mode of the PTA ligand. Hydrogen atoms, as well as the nitrate anions, are omitted for clarity.

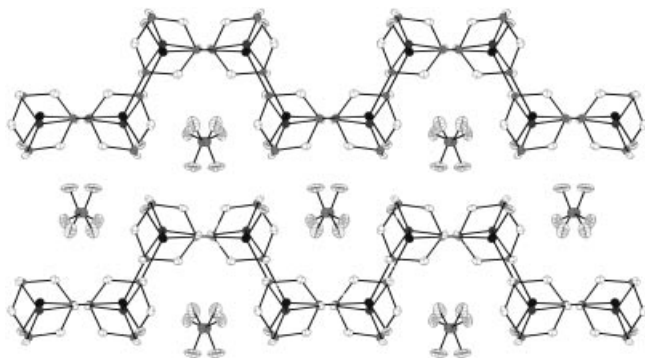


Figure 4. View of $[\text{Ag}(\text{PTA})(\text{H}_2\text{O})]\text{NO}_3$ along the c -axis which shows three polymer nets and the nitrate anions located in the channels. Hydrogen atoms are omitted for clarity.

(HMT). A variety of $[\text{AgX}(\text{HMT})]$ complexes have been prepared and structurally characterised and, depending on the metal/HMT ratios, the solution pH and the type of counterions, many different two- and three-dimensional network polymers have been observed.^[11–13] In particular, the polymeric net structure of $[\text{Ag}(\text{NO}_3)(\text{HMT})]$ ^[14] is almost identical to that of $[\text{Ag}(\text{PTA})(\text{H}_2\text{O})]\text{NO}_3$, with the exception that a nitrate ligand is O -coordinated to the silver atom instead of a water molecule, hence the channels in the 3D network of $[\text{Ag}(\text{NO}_3)(\text{HMT})]$ are vacant. The Ag–P bond length in $[\text{Ag}(\text{PTA})(\text{H}_2\text{O})]\text{NO}_3$ [2.3822(12) Å] is shorter than the Ag–P distances in other silver(I) nitrate complexes that contain bulky phosphane ligands such as $[\text{Ag}(\text{NO}_3)(\text{PPh}_3)_2]$ and $[\text{Ag}(\text{NO}_3)\{\text{P}(m\text{-MeC}_6\text{H}_4)_3\}]$ [2.443(1) and 2.4128(8) Å, respectively].^[15] However, if the bulkiness of the phosphane group is decreased, the Ag–P bond length becomes shorter as is evident in $[\text{Ag}\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}_2]\text{NO}_3$, whose Ag–P bond length is 2.3832(9) Å.^[15] This bond length is very similar to that observed in $[\text{Ag}(\text{PTA})(\text{H}_2\text{O})]\text{NO}_3$ in this work, which illustrates the small steric bulk of PTA. The two Ag–N distances [2.441(4) and 2.468(4) Å] are slightly longer than those observed in $[\text{Ag}(\text{NO}_3)(\text{HMT})]$ [2.406(5) and 2.335(6) Å] and $[\text{CpRu}(\text{H}_2\text{O})(\mu\text{-}P,N\text{-PTA})_2\text{AgCl}_2]_n$ [2.423(6) Å].^[6]

In summary we present here the first example of a PTA ligand that adopts a tridentate, bridging P,N,N' -coordination mode, which results in a polymeric net structure that contains hexagonal cavities occupied by nitrate anions.

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- [1] D. J. Daigle, A. B. Pepperman Jr., S. L. Vail, *J. Heterocycl. Chem.* **1974**, *11*, 407.
- [2] A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, *Coord. Chem. Rev.* **2004**, *248*, 955–993.
- [3] B. Cornils and W. A. Herrmann (Eds.), *Aqueous-phase Organometallic Catalysis Concepts and Applications*, 1st ed., Wiley-VCH, Weinheim, **1998**.
- [4] F. Joó, *Aqueous Organometallic Catalysis*, Kluwer Academic Publishers, Dordrecht, **2001**.
- [5] B. J. Frost, C. M. Bautista, R. Huang, J. Shearer, *Inorg. Chem.* **2006**, *45*, 3481–3483.
- [6] C. Lidrissi, A. Romerosa, M. Saoud, M. Serrano-Ruiz, L. Gonsalvi, M. Peruzzini, *Angew. Chem. Int. Ed.* **2005**, *44*, 2568–2572.
- [7] R. Usón, A. Laguna, M. Laguna, J. Jiménez, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1991**, 1361–1365.
- [8] F. Mohr, S. Sanz, E. Cerrada, M. Laguna, *Organometallics* **2006**, *25*, 3084–3087.
- [9] F. Mohr, E. Cerrada, M. Laguna, *Organometallics* **2006**, *25*, 644–648.
- [10] Experimental details: A solution of AgNO_3 (0.108 g, 0.636 mmol) in water (10 mL) was treated with an aqueous solution of PTA (0.100 g, 0.636 mmol). The solution was left to stand in an open vessel for ca. 48 h, and colourless X-ray quality crystals of the complex were formed, which were isolated by filtration. Yield 0.085 g (41%). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, D_2O): $\delta = -77.81$ (broad, unresolved P–Ag coupling).

ling) ppm. ^1H NMR (400 MHz, D_2O): δ = 4.29 (d, J = 2.5 Hz, 6 H, CH_2N), 4.61 (AB quartet, 6 H, CH_2P) ppm. $\text{C}_6\text{H}_{14}\text{N}_4\text{O}_4\text{PAg}$ (345.05): calcd. C 20.89, H 4.09, N 16.24; found C 20.73, H 3.87, N 16.30. Crystal data: Formula = $\text{C}_6\text{H}_{14}\text{N}_4\text{O}_4\text{PAg}$. M = 345.05. Colourless plates, $0.08 \times 0.22 \times 0.22$ mm, orthorhombic. Space group = $Pbca$, a = 11.1798(4) Å, b = 11.3646(3) Å, c = 16.9315(6) Å. α , β , γ = 90.0°. V = 2151.21(12) Å³. Z = 8. $D_{\text{calcd.}}$ = 2.131 mg/m³. μ = 2.029 mm⁻¹. Temperature = 123(2) K. λ (Mo- K_α) = 0.71073 Å. $T(\text{SADABS})_{\text{min/max}}$ = 0.7591/1.000. $F(000)$ = 1376. $2\theta_{\text{min/max}}$ = 9.44/50.00. hkl range = -13 to 9, -13 to 13, -20 to 20. No. of reflections = 11401. No. of independent reflections = 1875 (R_{int} = 0.0326). R_1 = 0.0428, wR_2 = 0.0866, R_1 (all data) = 0.0518, wR_2 (all data) = 0.0911. GOF (all data) = 1.154. $\Delta\rho_{\text{max/min}}$ = 0.923/-0.661. Data were collected with an Oxford Diffraction XCalibur2 CCD diffractometer. The structure was solved by direct methods and refined by the full-matrix least-squares method

with SHELXTL-NT 6.1. CCDC-603984 contains 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.

- [11] M. L. Tong, S. L. Zheng, X. M. Chen, *Chem. Eur. J.* **2000**, *6*, 3729–3738.
- [12] S. L. Zheng, M. L. Tong, X. M. Chen, S. W. Ng, *J. Chem. Soc., Dalton Trans.* **2002**, 360–364.
- [13] S. Lu, S. Qin, Y. Ke, J. Li, H. Pei, S. Zhou, X. Wu, W. Du, *Cryst. Res. Technol.* **2004**, *39*, 89–93.
- [14] P. A. Michelet, B. Viossat, P. Khodadad, N. Rodier, *Acta Crystallogr. Sect. B* **1981**, *37*, 2171–2175.
- [15] C. W. Liu, H. Pan, J. P. Fackler Jr., G. Wu, R. E. Wasylshen, M. Shang, *J. Chem. Soc., Dalton Trans.* **1995**, 3691–3697.

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