metal-organic compounds

catena-Poly[[di-*μ*-chloro-bis[(triphenylphosphine)silver(I)]]-*μ*-2-amino-pyrimidine-*κ*²*N*¹:*N*³]

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In the title supramolecular complex, $[Ag_2Cl_2(C_4H_5N_3)(C_{18}H_{15}P)_2]_n$, a one-dimensional chain is formed by dimeric $\{Ag_2Cl_2(PPh_3)_2\}$ units bridged by 2-aminopyrimidine moieties. The Ag atoms are four-coordinate, with an $AgCl_2NP$ core. A crystallographic inversion centre is located in the centre of the Ag_2Cl_2 chelate ring, while the crystallographic twofold axis bisects the 2-aminopyrimidine ligand.

Comment

Recently, we have obtained a series of d^{10} metal Cu^I and Ag^I complexes containing triphenylphosphine and nitrogenous heterocyclic ligands (Jin, Long *et al.*, 1998; Jin, Xin *et al.*, 1998; Jin, Wang & Xin, 1999; Jin, Xin, Deng & Yu, 1999; Jin, Xin, Zhu & Li, 1999). Here, we report the crystal and molecular structure of $[Ag_2Cl_2(C_4H_5N_3)(PPh_3)_2]_n$, (I), which is the first Ag^I complex containing the bridging 2-aminopyrimidine (AMP) ligand. This work complements and extends our structural characterization of this series of compounds. We have also recently reported a similar infinite-chain Cu^I complex, namely $[Cu_2I_2(C_4H_5N_3)(PPh_3)_2]_n$, (II) (Jin *et al.*, 2000).

(I)
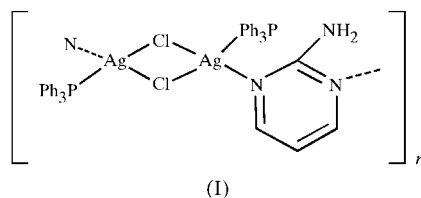
The object of our research is to synthesize supramolecular complexes using ligands which have the potential to bridge metal atoms. To date, supramolecular complexes reported in the literature have used a variety of bridging ligands. Both
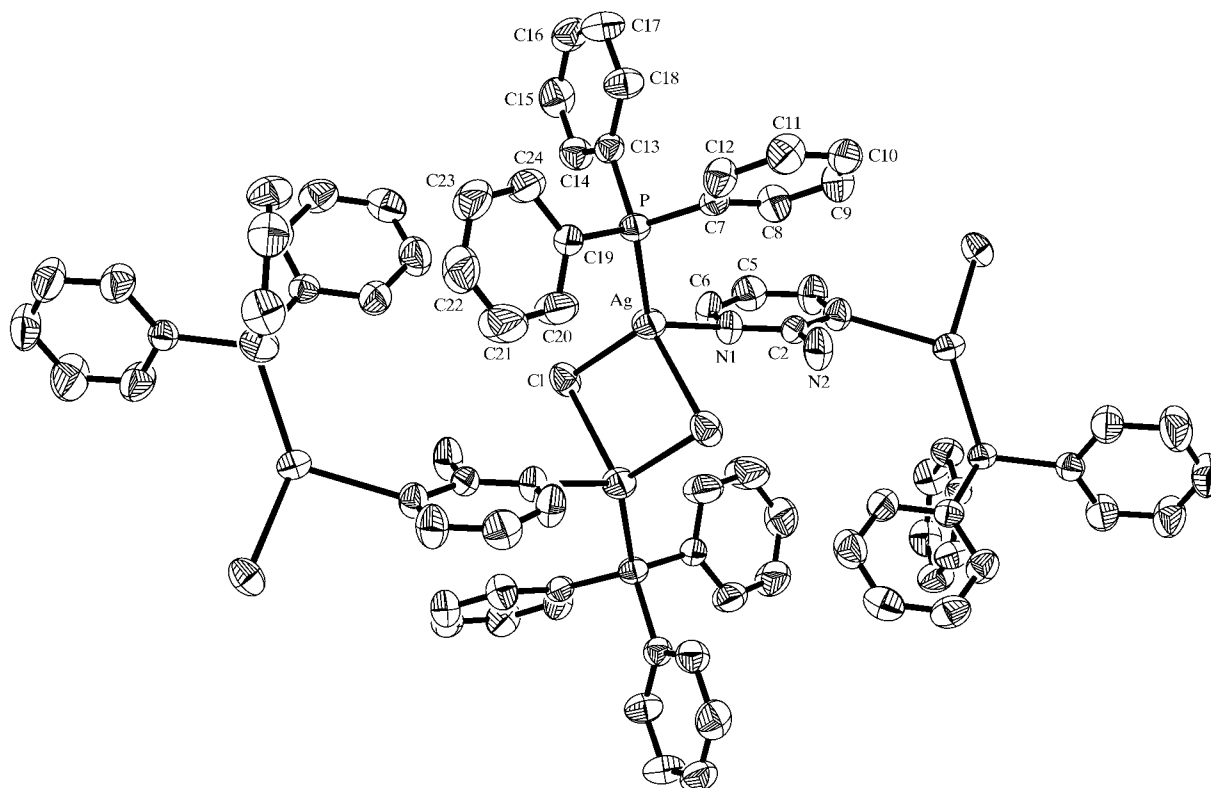

Figure 1
A view of the structure of (I). Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

inorganic anion ligands, such as S^{2-} (Huang *et al.*, 1997) and SO_4^{2-} (Lumme *et al.*, 1996), and neutral organic ligands, such as 4,4′-bipyridine (Lu *et al.*, 1997), pyrazine (Tong *et al.*, 1998) and AMP (Smith *et al.*, 1985; Jin *et al.*, 2000), have been used to synthesize supramolecular complexes.

The structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The compound has a one-dimensional chain structure, formed by two N atoms from the pyrimidine ring of the AMP ligand bridging two dimeric $\{Ag_2Cl_2(PPh_3)_2\}$ units. The pyrimidine ring N atoms are related by a crystallographic twofold axis which bisects the pyrimidine ring.

In the $[Ag_2Cl_2(C_4H_5N_3)(PPh_3)_2]$ unit of (I), the Ag atom is in the centre of a distorted coordination tetrahedron. Each Ag atom is coordinated to one P atom from PPh_3, two Cl atoms, and one N atom from the pyrimidine ring of AMP. As a result of the coordination of the N atom to Ag, the electric charge of AMP is transferred and the AMP molecules are isomerized to the carbamamidine structure, as indicated by the C2—N2 bond length of 1.329 (5) Å; this is similar to what is observed in (II). The Ag_2Cl_2 ring of (I), like the Cu_2I_2 ring of (II), is strictly planar.

The Ag—P distance is slightly shorter in (I) than in $[AgCl(PPh_3)_2]_2$, (III) (2.469 Å; Cassel, 1979) or $[AgXP-(C_6H_{11})_3]_2$ (X is Cl, Br or I; Bowmaker *et al.*, 1996). The Ag—Cl distances in (I) agree with those in (III) (2.669 Å). The Ag—N distance is slightly shorter in (I) than in $[AgCl(C_9H_7N)]_n$ (2.27 Å; Mills & White, 1984), or in $[AgI-(3-MeC_5H_4N)]$ [2.324 (7) Å], $[AgI(C_9H_7N)]_2$ [2.32 (2) Å] and $[AgI(2-MeC_5H_4N)]_2$ [2.352 (9) Å] (Healy *et al.*, 1983).

The Ag⋯Ag distance in (I) is significantly shorter than that in (III) [3.840 (2) Å], while the Cl⋯Cl distance of 4.210 (2) Å in (I) is significantly longer than that in (III) [3.710 (2) Å]. This is because PPh_3 is much bigger than AMP, so the effect of the additional steric hindrance of having two PPh_3 ligands coordinated to Ag in (III), compared with one PPh_3 and one AMP ligand in (I), results in the two Cl atoms being forced closer together, resulting in the longer Ag⋯Ag and shorter Cl⋯Cl distances, and larger Ag—Cl—Ag and smaller Cl—Ag—Cl angles observed in (III) compared with those in (I).

Experimental

The synthesis of (I) was carried out by the reaction of AgCl (0.143 g, 1 mmol), PPh_3 (0.26 g, 1 mmol) and 2-aminopyrimidine (0.10 g, 1 mmol) in CH_2Cl_2 solution (20 ml) at room temperature for 6 h. The solution was then filtered. White crystals of (I) were obtained by slow evaporation of a pale-red solution.

Crystal data

$[Ag_2Cl_2(C_4H_5N_3)(C_{18}H_{15}P)_2]$	$D_x = 1.587$ Mg m^{-3}
$M_r = 906.29$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 26
$a = 17.055$ (2) Å	reflections
$b = 16.642$ (4) Å	$\theta = 2.9–15.8°$
$c = 15.302$ (2) Å	$\mu = 1.29$ mm^{-1}
$\beta = 119.13$ (1)°	$T = 295$ (2) K
$V = 3793.9$ (11) Å^3	Prism, white
$Z = 4$	$0.46 \times 0.46 \times 0.40$ mm

Table 1
Selected geometric parameters (Å, °).

Ag—P	2.3981 (7)	Ag⋯Ag^i	3.2424 (7)
Ag—N1	2.402 (2)	Cl—Ag^i	2.7643 (8)
Ag—Cl	2.5451 (8)	N2—C2	1.329 (5)
Ag—Cl^i	2.7643 (8)		
P—Ag—N1	123.39 (6)	Cl—Ag—Cl^i	104.85 (2)
P—Ag—Cl	129.36 (3)	P—Ag⋯Ag^i	138.28 (2)
N1—Ag—Cl	91.26 (6)	N1—Ag⋯Ag^i	95.41 (5)
P—Ag—Cl^i	106.96 (3)	Cl—Ag⋯Ag^i	55.50 (2)
N1—Ag—Cl^i	95.18 (6)	Cl^i—Ag⋯Ag^i	49.354 (16)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2N⋯Cl^i	0.85 (3)	2.472 (13)	3.2954 (17)	164 (3)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.019$
ω scans	$\theta_{max} = 25.3°$
Absorption correction: empirical	$h = 0 \rightarrow 20$
(*SHELXTL*; Siemens, 1997)	$k = 0 \rightarrow 19$
$T_{min} = 0.518$, $T_{max} = 0.637$	$l = -18 \rightarrow 16$
3810 measured reflections	3 standard reflections
3429 independent reflections	every 97 reflections
2779 reflections with $I > 2\sigma(I)$	intensity decay: 1.4%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
$wR(F^2) = 0.058$	$\Delta\rho_{min} = -0.35$ e Å^{-3}
$S = 1.03$	Extinction correction: *SHELXL*97
3429 reflections	(Sheldrick, 1997)
294 parameters	Extinction coefficient: 0.00347 (11)
All H-atom parameters refined	
$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

The coordinates and equivalent isotropic displacement parameters for the H atoms were refined by difference Fourier synthesis [C—H distances are in the range 0.92 (3)–0.94 (1) Å]. The final difference Fourier maps showed highest and lowest electron densities of 0.36 and -0.35 e Å^{-3}, respectively.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

Bowmaker, G. A., Effendy & Harvey, P. J. (1996). *J. Chem. Soc. Dalton Trans.* pp. 2459–2465.

Cassel, A. (1979). *Acta Cryst.* B**35**, 174–177.

Healy, P. C., Mills, N. K. & White, A. H. (1983). *Aust. J. Chem.* **36**, 1851–1864.

Huang, Q., Wu, X. T. & Lu, J. X. (1997). *Chin. J. Struct. Chem.* pp. 253–257.

Jin, Q.-H., Long, D.-L., Wang, Y.-X. & Xin, X.-Q. (1998). *Acta Cryst.* C**54**, 948–949.

Jin, Q. H., Lu, X. M., Zhu, H. J. & Ji, X. P. (2000). *Chin. J. Chem.* **18**, 928–931.

Jin, Q.-H., Wang, Y.-X. & Xin, X.-L. (1999). *Acta Cryst.* C**55**, 341–343.

Jin, Q.-H., Xin, X.-L., Deng, Y.-H. & Yu, K.-B. (1999). *Acta Cryst.* C**55**, 860–863.

Jin, Q.-H., Xin, X.-L., Dong, C.-J. & Zhu, H.-J. (1998). *Acta Cryst.* C**54**, 1087–1089.

Jin, Q. H., Xin, X. L., Zhu, F. J. & Li, Y. (1999). *Z. Kristallogr.* **214**, 503–504.

Lu, J., Crisci, G., Niu, T. & Jacobson, A. J. (1997). *Inorg. Chem.* **36**, 5140–5141.

Lumme, P. O., Knuuttila, H. & Lindell, E. (1996). *Acta Cryst.* C**52**, 51–56.

Mills, N. K. & White, A. H. (1984). *J. Chem. Soc. Dalton Trans.* pp. 225–228.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Siemens (1991). *XSCANS User's Manual.* Version 2.10b. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1997). *SHELXTL.* Release 5.10. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Smith, G., O'Reilly, E. J., Kennard, C. H. L. & White, A. H. (1985). *J. Chem. Soc. Dalton Trans.* pp. 243–251.

Tong, M. L., Chen, X. M., Yu, X. L. & Mak, T. C. W. (1998). *J. Chem. Soc. Dalton Trans.* pp. 5–6.