metal-organic compounds

catena-Poly[[(N,N-dimethylformamide-κO)(nitrato-κO)silver(I)]-μ-1,2-bis(diphenylphosphino)ethane-κ²P:P'] at 100 and 293 K: temperature effects on the volume of the solvent pocket

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In the title chain compound, $[Ag(NO_3)(C_3H_7NO)(C_{26}H_{24}P_2)]_n$, the bis(diphenylphosphino)ethane (dppe) components lie across centres of inversion. The dppe units link the Ag^+ ions into chains along [100]. A nitrate anion is coordinated to the Ag atom, together with one molecule of N,N-dimethylformamide (DMF) solvent. At room temperature, the coordinated DMF shows a long Ag—O distance [2.620 (3) Å] and relatively large thermal motion, while at 100 K the Ag—O distance is shorter [2.5588 (19) Å] and the thermal motion is similar to that of the rest of the complex. The behaviour of the DMF molecule is related to the size of the solvent pocket, viz. 146 Å³ at 293 K and 131 Å³ at 100 K.

Comment

Bis(diphenylphosphino)ethane (dppe) is a versatile ligand, forming complexes in which a bridging motif is frequently encountered. In complexes with a reduced number of ligands, the result is the formation of a polymeric chain. Silver(I) is a particular example where diphosphine-bridged coordination polymers are common (Zhang et al., 2003; Aslanidis et al., 2004; Cingolani et al., 2006; Bao et al., 2005).

The structure of the title compound, (I), at 293 K is polymeric, with dppe ligands bridging between Ag centres to generate a chain. There are two half dppe ligands in the asymmetric unit, with the remaining parts being generated by crystallographic centres of inversion at the mid-points of the C—C bond of the ethane group (Fig. 1). The polymeric chains extend parallel to the crystallographic a axis (Fig. 2).

The Ag atom in (I) has a distorted tetrahedral geometry, made up of atoms P1 and P2 of the two half dppe ligands, atom O1 of the coordinating nitrate ligand and atom O11 of the N,N-dimethylformamide (DMF) molecule. The bond

distances and angles in (I) at 293 K (Table 1) are close to the average values observed in similar Ag complexes found in the Cambridge Structural Database (Version 5.27, August 2006;

(I)
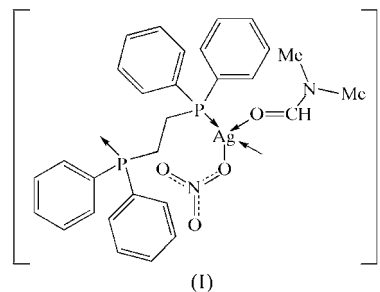
Allen, 2002), where the average Ag—P distance for Ag(dppe) complexes is 2.464 (6) Å (67 observations) and that for $Ag(NO_3)$ is 2.498 (9) Å (188 observations). The nitrate ligand shows a fairly long Ag1···O2 contact but with an acute N1—O2···Ag1 angle. This interaction forces the P1—Ag—P2 angle to open considerably. The other angles around the Ag are close to the ideal value of 109.47°.

The large thermal motion of the DMF solvate at room temperature prompted us to investigate the solid-state behaviour at low temperature. The single-crystal X-ray experiment at 100 K showed a slight reduction in the cell volume of 2.87%, corresponding to 42.19 (10) Å³, with decreases in the lengths of all three cell axes compared with the 293 K experiment. The b axis shows a much greater decrease (1.71%) than the a or c axes (0.80 and 0.68%, respectively). The resulting structure (Fig. 3) is very similar to that at 293 K. The distances and
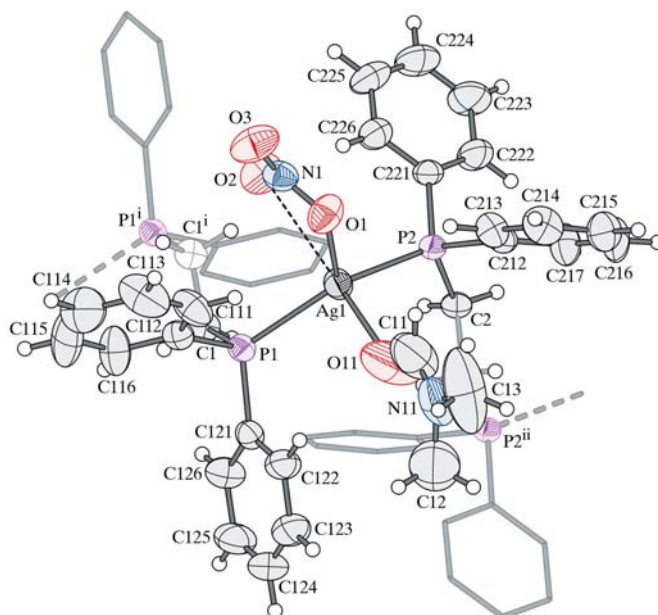

Figure 1
A view of (I) at 293 K, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The symmetry-generated part of the polymer is shown in grey, with phenyl groups represented as lines. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$.]

angles (Table 2) are very similar for the nitrate and dppe ligands and their bonds to the Ag centre. However, the DMF molecule not only presents anisotropic displacement parameters similar to the other ligand atoms, but also a much shorter Ag—O11 distance in the low-temperature study.

The volume of the solvent pocket was calculated using *PLATON* (Spek, 2003). At 293 K, one void was found per asymmetric unit, with a volume of 146 Å^3; the centroid has coordinates (0.197, 0.844, 0.034), 3.67 Å from atom C123, corresponding to the location of the DMF molecule (Fig. 4a).
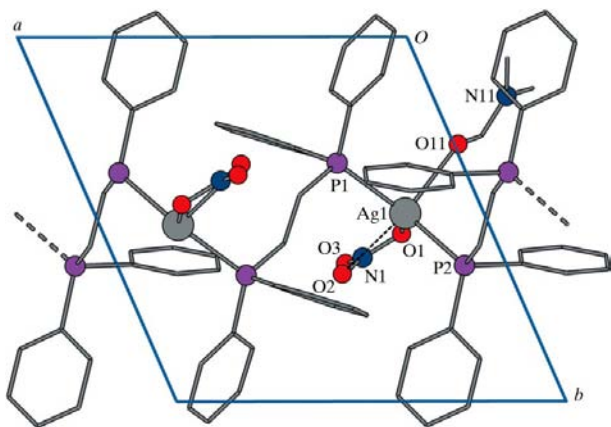

Figure 2
A view of the polymeric chain of (I). The vertical direction is parallel to the *b* axis and the horizontal direction is parallel to the *a* axis. The phenyl groups are represented as lines.
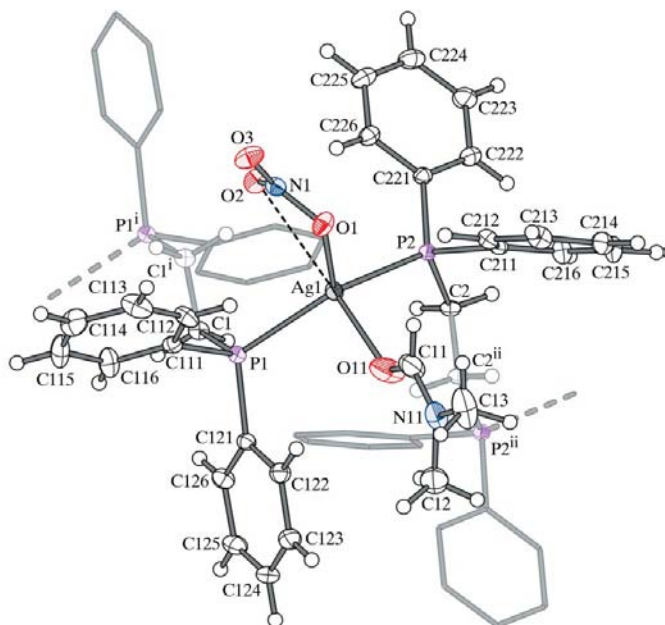

Figure 3
A view of (I) at 100 K, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The symmetry-generated part of the polymer is shown in grey, with phenyl groups represented as lines. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$.]
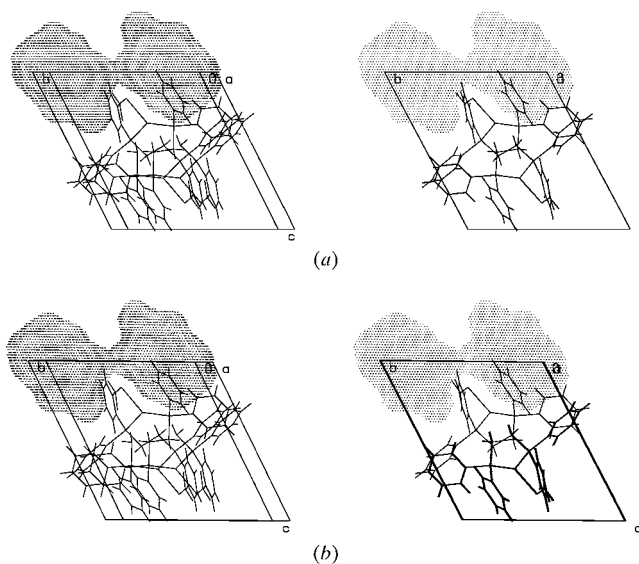

Figure 4
Stereoviews of the solvent pocket calculated by *PLATON* (Spek, 2003) at (a) 293 K and (b) 100 K. The vertical direction is parallel to the *b* axis and the horizontal direction is parallel to the *a* axis.

At 100 K, the volume of the void was found to be 132 Å^3, a decrease of 9.59%; the centroid has coordinates (0.197, 0.845, 0.034), 3.54 Å from atom C123. The volume of the DMF molecule in the solid state is about 119.7 Å^3 (Baburin & Blatov, 2004). At 293 K, the solvent pocket is much larger (26 Å^3) than the solvent, allowing greater motion. At 100 K, the cell-volume reduction is due largely to the reduction of the solvent pocket, restricting the motion of the DMF molecule. Concomitantly, the DMF molecule forms a shorter and stronger bond to the Ag centre.

Experimental

Compound (I) at 293 K

Crystal data

[Ag(NO$_3$)(C$_3$H$_7$NO)(C$_{26}$H$_{24}$P$_2$)]	V = 1466.34 (7) Å^3
M_r = 641.37	Z = 2
Triclinic, $P\bar{1}$	D_x = 1.453 Mg m^{-3}
a = 11.1758 (3) Å	Mo $K\alpha$ radiation
b = 12.1731 (3) Å	μ = 0.83 mm^{-1}
c = 13.0499 (3) Å	T = 293 (2) K
α = 112.201 (1)°	Block, colourless
β = 102.200 (1)°	0.26 × 0.15 × 0.08 mm
γ = 106.856 (1)°	

metal-organic compounds

Data collection

Bruker APEXII CCD area-detector diffractometer
φ and ω scans
Absorption correction: numerical; *APEX2* routines (*XPREP* and *SADABS*; Bruker, 2006) were used to perform the Gaussian

face-indexed numerical absorption correction
$T_{min} = 0.898$, $T_{max} = 0.951$
35945 measured reflections
8523 independent reflections
5657 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 30.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.111$
$S = 1.04$
8523 reflections
345 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.249P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I) at 293 K.

Ag1—O1	2.469 (2)	Ag1—P1	2.4445 (7)
Ag1—O2	2.851 (3)	Ag1—P2	2.4372 (7)
Ag1—O11	2.620 (3)		
P2—Ag1—P1	140.92 (2)	P1—Ag1—O11	95.27 (8)
P2—Ag1—O1	107.16 (6)	O1—Ag1—O11	84.19 (12)
P1—Ag1—O1	110.04 (6)	N1—O2—Ag1	87.55 (19)
P2—Ag1—O11	100.02 (11)	N1—O1—Ag1	105.46 (18)

Compound (I) at 100 K

Crystal data

[Ag(NO$_3$)(C$_3$H$_7$NO)(C$_{26}$H$_{24}$P$_2$)]
$M_r = 641.37$
Triclinic, $P\bar{1}$
$a = 11.0869$ (3) Å
$b = 11.9653$ (4) Å
$c = 12.9618$ (4) Å
$\alpha = 112.322$ (2)°
$\beta = 102.410$ (2)°
$\gamma = 106.216$ (2)°

$V = 1424.15$ (9) Å^3
$Z = 2$
$D_x = 1.496$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.86$ mm^{-1}
$T = 100$ (2) K
Block, colourless
$0.22 \times 0.15 \times 0.06$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
φ and ω scans
Absorption correction: numerical; *APEX2* routines (*XPREP* and *SADABS*; Bruker, 2006) were used to perform the Gaussian

face-indexed numerical absorption correction
$T_{min} = 0.900$, $T_{max} = 0.958$
36255 measured reflections
8237 independent reflections
7005 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 30.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.081$
$S = 1.04$
8237 reflections
345 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 1.2423P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.60$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (I) at 100 K.

Ag1—O1	2.4451 (16)	Ag1—P1	2.4354 (5)
Ag1—O2	2.8573 (17)	Ag1—P2	2.4268 (6)
Ag1—O11	2.5588 (19)		
P2—Ag1—P1	139.863 (18)	P1—Ag1—O11	95.67 (5)
P2—Ag1—O1	107.38 (4)	O1—Ag1—O11	83.44 (7)
P1—Ag1—O1	110.53 (4)	N1—O2—Ag1	86.18 (12)
P2—Ag1—O11	101.31 (6)	N1—O1—Ag1	105.41 (12)

All H atoms were located in difference maps and were then placed in idealized positions and treated as riding atoms, with C—H distances of 0.93 (aromatic and aldehyde), 0.97 (CH$_2$) or 0.96 Å (CH$_3$) at 293 K, and 0.95, 0.99 and 0.98 Å, respectively, at 100 K, with $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl groups and 1.2 for all other H atoms.

For both compounds, data collection: *APEX2*, *BIS* and *COSMO* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT* and *SADABS* (Bruker, 2006); program(s) used to solve structure: *SHELXTL* (Bruker, 2006); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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