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The silver(I) coordination polymer $[AgO_2PPh_2]_n$ and unsupported Ag···Ag interactions derived from aminophosphinate and phosphinic acid

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ABSTRACT

The ligand N-*tert*-butyl-1,1-diphenylphosphinamine, Ph_2P-N(H)CMe_3, was prepared from *tert*-butylamine and diphenylchlorophosphine. The phosphine portion of the ligand became partially oxidized in air to form $Ph_2P(O)N(H)CMe_3$, **L1**, whilst further oxidation led to diphenylphosphinic acid, $Ph_2P(O)OH$. X-ray analysis revealed that ligand **L1** was isolated in the solid-state in a dimeric polymorphic form, different from the previously reported trimeric form. Ligand **L1** was subsequently treated with solid $AgSO_3CF_3$ in THF which formed a rare silver(I) dinuclear complex of the type $[Ag(CF_3SO_3)\{OPPh_2N(H)CMe_3\}_2\{Ag(OPPh_2N(H)CMe_3)_2\}]SO_3CF_3$, **1**, and consists of ligand unsupported Ag···Ag interactions of 2.89 Å coordinating through two O donor atoms from the two separate silver units (A and B) and with no coordination through the N atom. Further, silver unit A contains a 3-coordinate Ag(I) center, bent significantly from a linear geometry due to interaction from the triflate O donor atom, whilst unit B remained essentially 2-coordinate and linear. The diphenylphosphinate reacted with solid $AgSO_3CF_3$ in THF at room temperature and this led to an unusual Ag(I) coordination polymer, $[Ag_2\{(\mu\text{-}O)OPPh_2\}\{O_2PPh_2\}]_n$ **2**, consisting of two different bonding modes of O-donor atoms in a 4-coordinate arrangement around the Ag(I) center. Compounds **L1**, **1** and **2** were all obtained in moderate to good yields, and analyzed by single crystal X-ray studies, solution ^1H and ^{31}P NMR, IR, and elemental analyses.

1. Introduction

The metallophilic interactions between closed-shell d^{10} metal ions of the coinage metals (Cu, Ag, Au) often have a strong structural and directional influence affecting the optical and electronic properties of such complexes [1]. This phenomenon is frequently observed in gold(I) complexes, with the term "aurophilicity" being used to describe Au(I)···Au(I) interactions that theorists have attribute to correlation and relativistic effects [2]. Silver(I), the lighter, but not necessarily smaller [3] group 11 metal congener, has diminished relativistic effects [4] but a significant number of complexes with weak Ag(I)···Ag(I) interactions, termed "argentophilicity", has been observed [5]. Argentophilic interactions can be further divided amongst the majority of ligand supported [6], and a few ligand unsupported [7] types. Argentophilic interactions also contributes to the formation of diverse Ag(I) geometries, including simple tetrahedron [8] discrete octa- and decanuclear silver clusters [9], triangulated dodecahedrons [10] and hexacapped trigonal bipyramids [11], amongst others. However, in contrast to the large number of cyclic and polyhedral Ag(I) aggregates, those with linear geometries are more scarce [12] although a common observation here is the formation of 1D infinite Ag(I) nanowires [13]. A number of elegant crystal engineered Ag(I) supramolecular frameworks and coordination complexes are known containing both supported and unsupported weak Ag(I)···Ag(I) interactions [14]; the latter can also be extended to cationic systems [15]. The majority of ligand types used to engender Ag(I)···Ag(I) interactions include carboxylic type spacers [16] including a trapped carbonate ion derived from atmospheric CO_2 [17]. Three different types of coordination polymers, one-dimensional (1D) straight chain, 1D-columnar structure, and two-dimensional (2D) layer structure, have been prepared by the complexation of Ag(I) ions with bis(pyridyl) ligands linked by an aromatic sulfonamide [18].

In contrast to O-donor carboxylates and N-donor pyridyls and pyrazoles, the chemistry of phosphine chalcogenide silver(I) complexes have been less explored, even though silver displays an ability to coordinate readily to both hard and soft donor atoms. The first examples of silver phosphonites contained no X-ray structural

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reports, but it was found the reactions between metal halides, metal carbonyl halides, or metal olefin halides, and dialkyl phenylphosphonite ligands performed in polar solvents afforded a general route to an extensive series of uncharged complexes [19]. The versatility of the iminodiphosphine chalcogenide species $[R_2P(E)HNP(E)R_2]$ (E = O, S, Se) renders them excellent ligand scaffolds with which to probe the hard–soft behaviour of silver(I) [20]. Silver phosphinates have been used in catalysis for direct annulations toward phosphorylated oxindoles [21] and a tetrasilver(I) phosphonitocavitand [22] and silver(I) phosphonates have been synthesized [23]. Structures and ligand conformations of Ag(I) complexes containing phosphinic amide ligands have been reported [24] as well as structural characterization of some arylamidinium diphenylphosphinates forming one-, two- and three-dimensional networks by charge-assisted hydrogen bonds and through the interaction of $AgSO_3CF_3$ [25]. Thin films of silver metal were deposited from tetraphenyldioxoimidodiphosphinato silver(I) [26]. The N-aminodiphenylphosphine class of compounds has been known for over 50 years [27] together with its oxidation behavior toward oxygen and sulfur [28] and the facile acidic cleavage of the P–N bond [29].

Ironically, although AgO_2PPh_2 is often used as an $O_2PPh_2^-$ transfer reagent [30], it appears the present study reports the solid-state structure of AgO_2PPh_2 itself for the first time. In our ongoing studies of phosphor-1,1-dichalcogenates and aminophosphines of group 11 metals [31], we report (i) a new dimeric polymorph of an aminodiphenylphosphine derivative, an (ii) unusual ligand unsupported silver(I) dinuclear complex containing the $OPPh_2N(H)CMe_3$ ligand and stabilized by triflate, and (iii) the coordination polymer of AgO_2PPh_2 containing different Ag–Ag, Ag–O and P–O bonding modes.

2. Experimental

2.1. General

Unless otherwise stated, all reactions were carried out under an inert atmosphere of positive nitrogen gas flow using standard Schlenk techniques. Reactions were stirred magnetically with a Teflon coated stirrer-bar. Glassware was dried for 24 h at 160 °C and assembled hot under a stream of dinitrogen gas. Diethyl ether, tetrahydrofuran, and hexane were distilled over sodium wire using a benzophenone-ketyl radical indicator. Dichloromethane was distilled over anhydrous calcium hydride. Room temperature refers to 23–25 °C; higher temperatures were obtained with the use of a silicone-based oil bath. The following chemicals were purchased from the Sigma–Aldrich company: chlorodiphenylphosphine, t-butyl amine and silver trifluoromethanesulfonate. Deuterated solvents were obtained from Merck. Nitrogen gas was obtained from Afrox, South Africa.

2.2. Preparation of $Ph_2P(O)N(H)CMe_3$, (**L1**)

In a Schlenk tube, t-butylamine (0.332 g, 4.53 mmol) was added to diethyl ether (30 mL) with stirring. The solution was immersed into a dry ice/acetone bath at −78 °C and n-BuLi (2.84 mL, 1.6 M, 4.54 mmol) was added drop-wise and stirred for 20 min. Chlorodiphenylphosphine (0.974 g, 4.415 mmol) in diethyl ether (40 mL) was added slowly to the lithiated solution and stirred for 20 min. The reaction was gradually warmed to room temperature and stirred for 20 min. The solvent volume was reduced and the LiCl by-product was filtered off using a Büchner apparatus under vacuum (presumably aerial oxidation at the P atom occurred during this step). The filtrate was pumped down under reduced pressure which resulted in a white solid. Yield: 0.826 g, 70%; Melting point: 133–136 °C. ^1H NMR, $(CDCl_3)$, δ (ppm): 1.29 (1H, s, NH), 1.27 (9H, s, t-Bu), 7.33 (8H, m, Ph), 7.41 (2H, dd, Ph, J_{H-H} = 6.72, 1.54 Hz). ^{13}C NMR, $(CDCl_3)$, δ (ppm): 32.28 (CH_3), 53.09 $(\underline{C}Me_3)$, 128.30 (ortho-ArC), 131.74 (meta-ArC), 135.70 (para-ArC). ^{31}P NMR, $(CDCl_3)$, δ: 19.51 ppm. *Anal.* Calc. for $C_{16}H_{20}NOP$: C, 70.31; H, 7.38; N, 5.12. Found: C, 70.40; H, 7.32; N, 5.08%. Selected IR data ν/cm^{-1}: 1175 (s), 1109(s), 692 (s), 522 (s).

2.3. Preparation of $Ag(CF_3SO_3)\{OPPh_2N(H)CMe_3\}_2\{Ag(OPPh_2N(H)CMe_3)_2\}]SO_3CF_3$ (**1**)

To a solution of **L1** (0.394 g, 0.496 mmol) in THF (20 mL), silver trifluoromethanesulfonate (0.0646 g, 0.251 mmol) was added, the Schlenk tube was covered in foil to protect materials from light sources. The mixture was stirred for 4 h at room temperature and solvent was removed under reduced pressure. Dichloromethane was added and stirred for an additional 10 min, and filtered through anhydrous $MgSO_4$. Solvent was removed in vacuo to obtain a white powder. Yield: 0.134 g, 68% yield. Melting point: 147–149 °C. ^1H NMR, $(CDCl_3)$, δ (ppm): 1.64 (4H, s, NH), 1.30 (36H, s, t-Bu), 7.44 (32H, m, Ph), 7.89 (8H, dd, Ph, J_{H-H} = 6.68, 1.20 Hz). ^{13}C NMR, $(CDCl_3)$, δ (ppm): 32.29 (CH_3), 53.00 $(\underline{C}Me_3)$, 128.29 (ortho-ArC), 131.42 (meta-ArC), 135.70 (para-ArC). ^{31}P NMR, $(CDCl_3)$, δ: 19.49 ppm. *Anal.* Calc. for $C_{62}H_{76}Ag_2F_6N_4O_{10}P_4S_2$: C, 47.89; H, 4.93; N, 3.60. Found: C, 47.90; H, 4.83; N, 3.68%. Selected IR data ν/cm^{-1}: 3181(m), 1172 (s), 1122(s), 678 (s), 542 (s).

2.4. Preparation of $[Ag_2\{(\mu\text{-}O)OPPh_2\}\{O_2PPh_2\}]$, (**2**)

A Schlenk tube was charged with a solution of *t*-butylamine (0.884 mL, 8.36 mmol) in THF (50 mL). A catalytic amount of DMAP (0.102 g, 0.836 mmol) was added, and the solution was allowed to stir for 5 min at room temperature. Triethylamine (1.800 mL, 12.54 mmol) was added and the solution was allowed to stir for a further 5 min. Upon addition of chlorodiphenylphosphine (1.500 mL, 8.36 mmol) a white precipitate formed, $Et_3N{\cdot}HCl$. The ensuing mixture was allowed to stir for approximately 3 h. The mixture was filtered through anhydrous $MgSO_4$ and Celite into a separate pre-weighed Schlenk tube. The solvent was removed *in-vacuo* and the Schlenk tube was re-weighed to determine the yield. Thereafter, 40 mL of THF with a pre-determined amount of $AgSO_3CF_3$ (2.14 g; 8.36 mmol) was added. The solution was allowed to stir for 30 min and solvent was removed *in vacuo*. Yield: 2.93 g, 54%; Melting point: 114–117 °C. ^1H NMR, $(CDCl_3)$, δ (ppm): 7.34 (8H, m, Ph), 7.44 (4H, t, Ph, J_{H-H} = 6.52 Hz), 7.69 (8H, dd, Ph, J_{H-H} = 12.60, 7.20 Hz). ^{13}C NMR, $CDCl_3$, δ (ppm): 128.28 (ortho-ArC), 131.23 (meta-ArC), 131.90 (para-ArC). ^{31}P NMR, $CDCl_3$, δ: 33.26 ppm. *Anal.* Calc. for $C_{48}H_{40}Ag_4O_8P_4$: C, 44.34; H, 3.10; O, 9.84. Found: C, 45.01; H, 3.25; O, 9.31%. Selected IR data ν/cm^{-1}: 3077(m), 174 (s), 1120(s), 689 (s), 519 (s).

2.5. Crystallography

Crystals were mounted on glass fibers with epoxy resin, and all geometric and intensity data were collected on a Bruker APEXII CCD diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data reduction was carried out with the SAINT-Plus software [32]. The SADABS program was used to apply an empirical absorption correction [33]. All structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL software package [34], found in SHELXTL/PC version 5.10 [35]. A complete listing of crystallographic data and parameters are reported in Table 5.

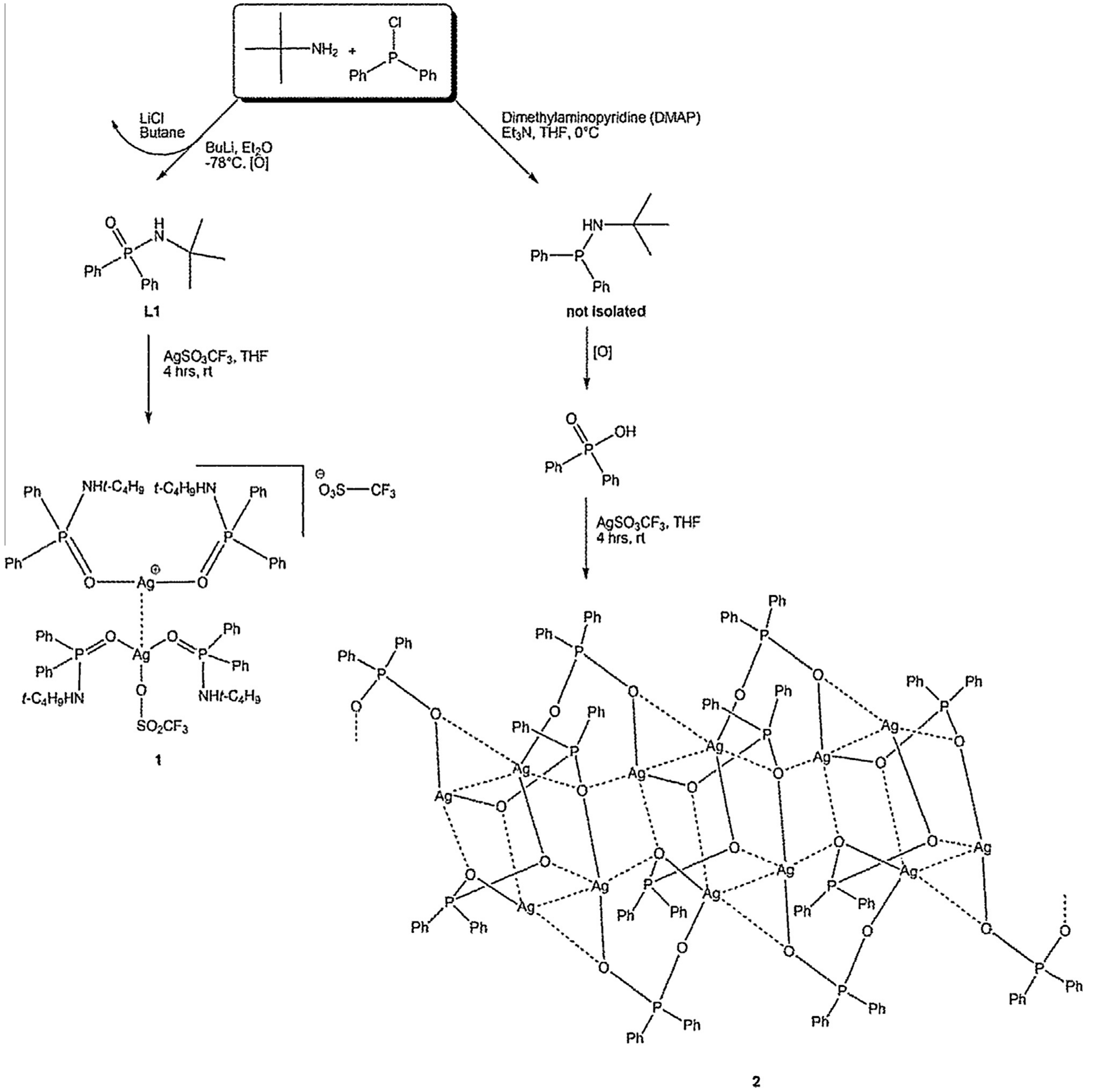
3. Results and discussion

3.1. $Ph_2P(O)N(H)CMe_3$, **L1**

The ligand **L1** was isolated as the aerially oxidized product of $(C_6H_5)_2PNH\text{-}t\text{-}C_4H_9$ in 70% yield, see Scheme 1. The precursor $(C_6H_5)_2PNH\text{-}t\text{-}C_4H_9$ was in turn prepared from the reaction between deprotonated *tert*-butylamine and diphenylchlorophosphine. The solid-state structure is a different polymorph from one previously reported [36] which contains three molecules in the asymmetric unit while the structure in the present study contains only two. The molecular structure of **L1**, shown in dimeric form and assembled through hydrogen bonds, is shown in Fig. 1.

The spatial difference between **L1** and its known polymorph can be observed through the overlay between the two molecules which yields a root mean square value of 1.84, which illustrates the large difference in the orientation of the molecules within their respective unit cells. Further expansion along the hydrogen bonding contacts of both **L1** and its polymorph revealed that the packing of both molecules differ, ie **L1** adopts a *zig-zag* orientation while the other polymorph adopts a closed circular orientation, see Fig. 2.

The solution structure of **L1** shows a single peak in the ^{31}P NMR spectrum at 19.51 ppm. The infrared spectrum shows a strong band at 1175 cm^{-1} assigned to a $\nu(P–O)$ stretching vibration. Initially, it was assumed that the starting chlorodiphenylphosphine was oxidised, but this was shown to be pure by ^{31}P NMR, hence oxidation either occurred aerially during the synthesis procedure, but we suspect more likely during crystal growing manipulations because all subsequent spectroscopies and elemental analysis were determined from the obtained microcrystalline materials.



Scheme 1. Formation of N-*tert*-butyl-diphenylphosphinic amide ligand (**L1**), $[Ag(CF_3SO_3)(OPPh_2N(H)CMe_3)_2\}\{Ag(OPPh_2N(H)CMe_3)_2\}]SO_3CF_3$ (**1**), and $[Ag_2\{(\mu\text{-}O)OPPh_2\}\{O_2PPh_2\}]$, (**2**).

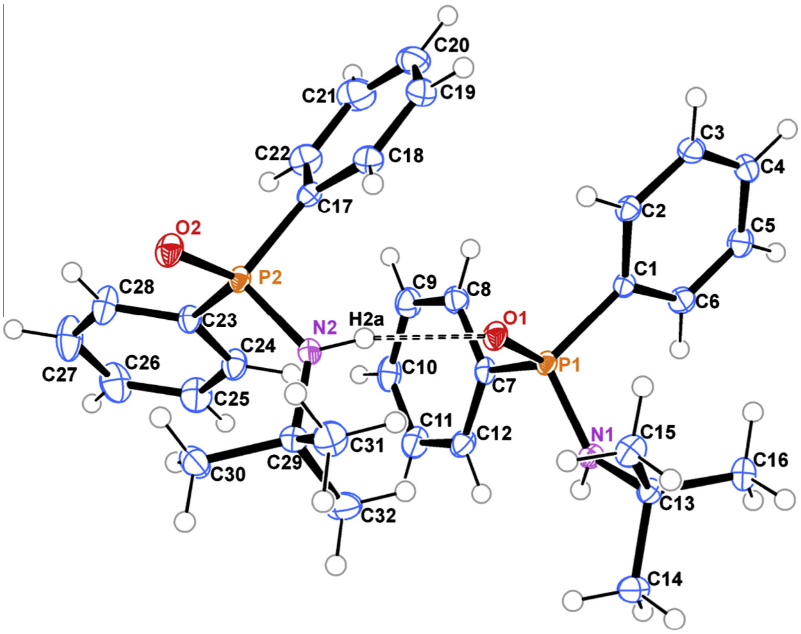


Fig. 1. Ligand **L1** shown as dimer with atom labeling. The displacement ellipsoids are shown at the 50% probability level.

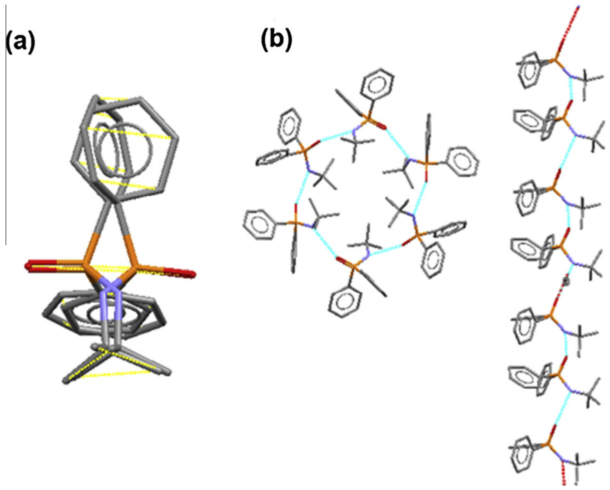


Fig. 2. (a) Overlay of previously reported polymorph [36] and **L1**, (b) closed circular orientation (left) compared with *zig-zag* orientation (right) for **L1**. Hydrogen bonding interactions dictate both polymorphic structures.

The solid-state structure crystallized in a triclinic space group $P\bar{1}$ and contains two molecules in the asymmetric unit linked together by hydrogen bonding, with the unit cell containing four ligand molecules. In **L1**, the two asymmetric units are assembled through the N(2)–H(2A)···O(1) hydrogen bonding interaction, in the structure, the dimeric units are in turn held together by a network of weak N(1)–H(1)···O(2) interactions, see Fig. 1 and Table 1. The two molecules within the asymmetric unit interact *via* both intra- and intermolecular hydrogen bonding interactions. The two molecules in the asymmetric unit have virtually the same bonding parameters, see Table 2. The geometry of each P atom can be described as a distorted tetrahedron as seen by angles O(1)–P(1)–C(1) and O(1)–P(1)–N(1) as 109.51(5)° and 115.29(5)°, respectively, around the P(1) center, and O(2)–P(2)–C(23) and O(2)–P(2)–N(2) as 108.77(5)° and 117.15(5)°, respectively, around P(2). The P=O bond lengths for the two molecules are 1.4900(8) and 1.4911(9) Å respectively, and is in good agreement with the literature values of the similar compounds [36]. The P–N and P–C bond distances are comparable to similar compounds from literature [36–38].

Table 1
Hydrogen-bonding interactions.

D–H···A (Å)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N(2)–H(2A)···O(1)	0.88	2.03	2.8891 (13)	172
N(1)–H(1)···O(2)	0.88	2.28	2.8932 (13)	127

3.2. *[Ag(CF$_3$SO$_3$){OPPh$_2$N(H)CMe$_3$}$_2${Ag(OPPh$_2$N(H)CMe$_3$)$_2$]SO$_3$CF$_3$, (**1**)*

The reaction between [OP(C$_6$H$_5$)$_2$(NH-*tert*-C$_4$H$_9$)] (**L1**) and AgSO$_3$CF$_3$ in THF led to the formation of a novel dinuclear silver(I) complex and consists of a ligand unsupported weak Ag···Ag interactions coordinating through two O donor atoms from the two separate silver units (A and B) and with no coordination

Table 2
Selected bond lengths (Å) and angles (°) for **L1**.

N(1)–P(1)	1.6434(10)	P(2)–N(2)–H(2A)	115.5
N(1)–H(9)	0.8800	O(1)–P(1)–N(1)	115.29(5)
N(2)–P(2)	1.6357(10)	O(1)–P(1)–C(7)	112.71(5)
N(2)–H(2A)	0.8800	N(1)–P(1)–C(7)	103.33(5)
P(1)–O(1)	1.4900(8)	O(1)–P(1)–C(1)	109.51(5)
P(2)–O(2)	1.4911(9)	N(1)–P(1)–C(1)	109.81(5)
C(23)–P(2)	1.8080(12)	C(7)–P(1)–C(1)	105.65(5)
C(13)–N(1)	1.4898(14)	O(2)–P(2)–N(2)	117.15(5)
C(7)–P(1)	1.8073(12)	O(2)–P(2)–C(17)	112.96(5)
C(1)–P(1)	1.8112(11)	N(2)–P(2)–C(17)	101.05(5)
		O(2)–P(2)–C(23)	108.77(5)
		N(2)–P(2)–C(23)	108.23(5)
		C(17)–P(2)–C(23)	108.18(5)
		C(29)–N(2)–P(2)	128.98(8)
		C(13)–N(1)–P(1)	126.99(7)
		C(13)–N(1)–H(1)	116.5
		P(1)–N(1)–H(1)	116.5
		N(1)–C(13)–C(14)	105.96(9)
		N(1)–C(13)–C(15)	111.80(9)
		C(2)–C(1)–P(1)	119.63(9)
		C(6)–C(1)–P(1)	120.77(9)

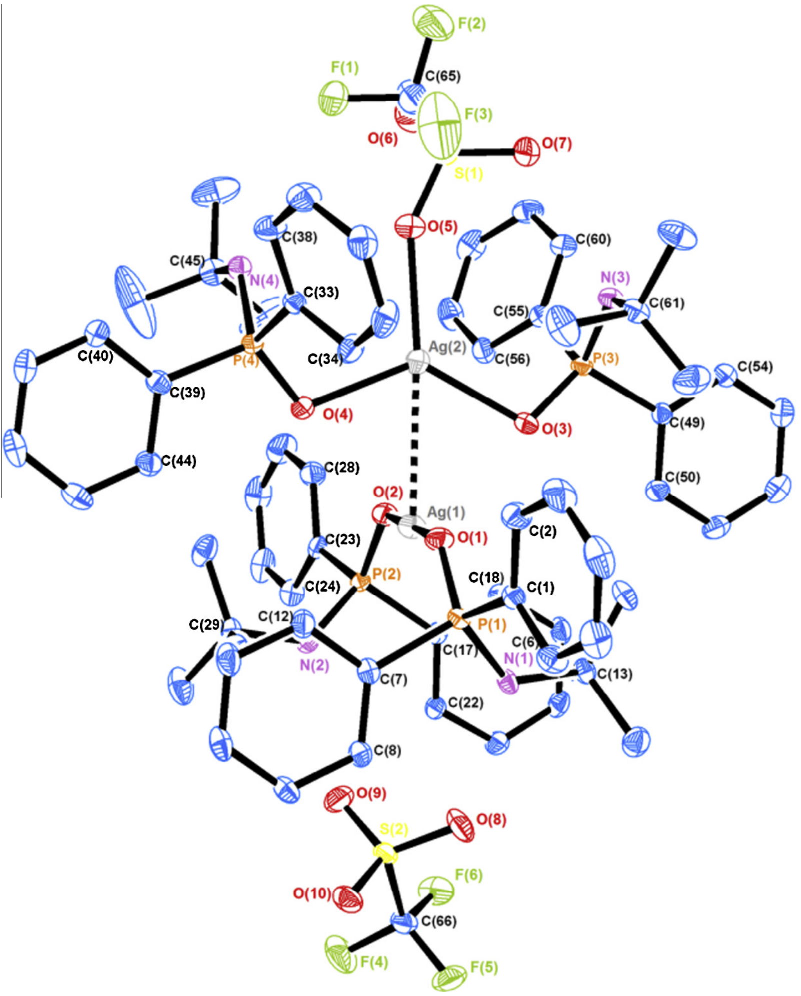


Fig. 3. Complex **1** showing the atom labeling. The displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are excluded for clarity.

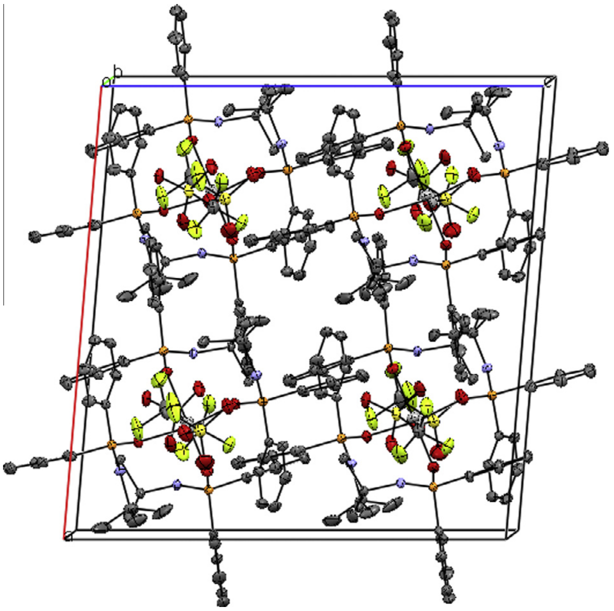


Fig. 4. Packing diagram of **1** seen along the *b* axis.

Table 3
Selected bond lengths (Å) and angles (°) for complex **1**.

Ag(1)–Ag(2)	2.8979(3)	O(5)–Ag(2)–Ag(1)	174.67(5)
O(5)–Ag(2)	2.370(2)	O(4)–Ag(2)–Ag(1)	66.89(4)
O(5)–S(1)	1.449(2)	O(3)–Ag(2)–Ag(1)	63.11(4)
O(4)–Ag(2)	2.2475(18)	O(4)–Ag(2)–O(5)	107.77(7)
O(4)–P(4)	1.5107(18)	O(3)–Ag(2)–O(5)	122.20(7)
O(3)–Ag(2)	2.2472(18)	O(3)–Ag(2)–O(4)	129.68(6)
O(3)–P(3)	1.5115(18)	O(2)–Ag(1)–Ag(2)	85.82(5)
O(2)–Ag(1)	2.1011(19)	O(1)–Ag(1)–Ag(2)	94.19(5)
O(2)–P(2)	1.5091(18)	O(1)–Ag(1)–O(2)	179.56(8)
O(1)–Ag(1)	2.0900(18)	C(7)–P(1)–C(1)	108.74(10)
O(1)–P(1)	1.5076(18)	N(1)–P(1)–C(1)	110.20(11)
N(4)–P(4)	1.648(2)	O(1)–P(1)–C(1)	105.14(11)
N(3)–P(3)	1.655(2)	N(1)–P(1)–C(7)	103.71(10)
N(2)–P(2)	1.633(2)	O(1)–P(1)–C(7)	109.71(11)
N(1)–P(1)	1.630(2)	O(1)–P(1)–N(1)	119.09(11)
C(1)–P(1)	1.802(2)	S(1)–O(5)–Ag(2)	150.98(14)
		P(4)–O(4)–Ag(2)	110.16(9)
		P(3)–O(3)–Ag(2)	107.33(9)
		P(2)–O(2)–Ag(1)	118.24(11)
		P(1)–O(1)–Ag(1)	122.56(11)

through the N atom. Further, silver unit A contains a 3-coordinate Ag(I) center, bent significantly from a linear geometry due to interaction from the triflate O donor atom, whilst unit B remained

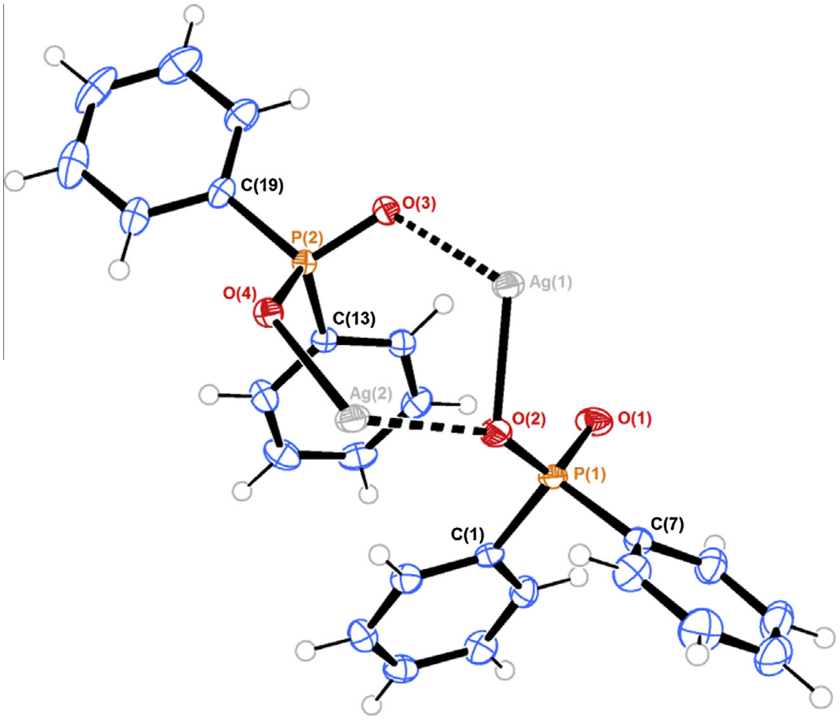


Fig. 5. Asymmetric unit of complex **2** showing atom labeling. The displacement ellipsoids are shown at the 50% probability level.

Table 4
Selected Bond lengths (Å) and angles (°) for complex **2**.

Ag(1)–Ag(2)	3.1596(2)	O(3)–Ag(1)–Ag(2)	171.77(3)
Ag(1)–O(2)	2.2274(13)	Ag(1)–Ag(2)–O(1)	142.54(4)
Ag(1)–O(3)	2.5133(13)	Ag(1)–O(2)–Ag(2)	86.13(5)
Ag(1)–O(4)c	2.3343(13)	O(3)–Ag(1)–O(4)c	83.09(4)
Ag(1)–O(3)d	2.3418(12)	O(3)–Ag(1)–O(3)d	87.63(4)
Ag(2)–O(2)	2.3962(13)	O(4)c–Ag(1)–O(3)d	100.93(4)
Ag(2)–O(4)	2.3349(13)	O(3)–P(2)–C(19)	108.95(8)
Ag(2)–O(1)a	2.2058(14)	C(13)–P(2)–C(19)	108.13(8)
Ag(2)–O(3)c	2.5044(13)	O(4)–P(2)–C(19)	107.75(8)
P(1)–O(1)	1.4982(13)	O(3)–P(2)–O(4)	115.90(7)
P(1)–O(2)	1.5120(13)	O(1)–P(1)–O(2)	118.25(8)
P(1)–C(1)	1.8010(18)		
P(1)–C(7)	1.807(2)		
P(2)–O(3)	1.5144(13)		
P(2)–O(4)	1.5178(13)		
P(2)–C(13)	1.8010(18)		
P(2)–C(19)	1.802(2)		

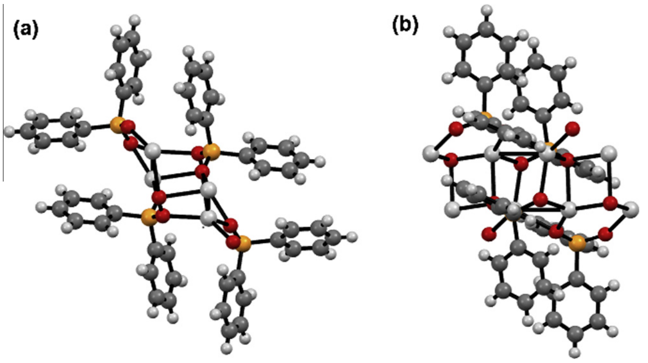


Fig. 6. Complex **2** seen along the (a) *a* axis (b) *c* axis.

essentially 2-coordinate and linear, see Scheme 1. Note that in the preparation method a 1:1 M ratio was initially used in an attempt to form metallacyclic neutral dinuclear silver(I) complex with an anionic bridging O–P–N ligand of the type [$Ag_2(OPPh_2NCMe_3)_2$], following deprotonation with triflate. This was based on the assumption that the N atom would be activated, either in protonated or deprotonated form. Clearly the conditions demanded a M:L ratio of 1:2 instead, completely bypassing any N donor coordination with the metal, and with triflate ions being retained in the structure. This caused a significant reduction of overall yield (35%). Given that Ag(I) can easily bind non-bulky N donor ligands, in hindsight one may speculate that the N lone-pair electrons in this case is sterically hindered by the combination of t-butyl group and phenyl rings, preventing coordination. Knowing the more efficient ratio to be 1:2, the experiment was repeated, affording a higher yield (68%). The characterized material corresponded with previously analysed data. The solution structures of **1** by both ^{1}H and ^{31}P NMR shows only a very slight shift when compared to the free **L1** ligand, suggesting the P=O–M dative coordinative bond is weak. The infrared spectrum of complex **1** showed distinct bands at 3181 and 1172 cm^{-1}, corresponding to M–O and P–O vibrational stretches, respectively.

Complex **1** crystallized in the monoclinic *Cc* space group. The argentophilic Ag(I)···Ag(I) interaction between the two Ag atoms is 2.8979(3) Å which coincides with previously reported bond distances in the range 2.869(5)–2.981(5) Å [39–41] and is also well below the sum of van der Waals radii of silver [42]. A number of different Ag-O bond lengths can be discerned. The longest is the Ag(2)–O(5) bond derived from the triflate O donor atom to the Ag atom, measuring 2.370(2) Å and also impacts on the geometry around the Ag(2) atom. By comparison, the distance between Ag(1) and O(9), with no triflate interaction, is *ca.* 5.078 Å. The geometry around the Ag(2) atom adopts a distorted trigonal planar geometry as suggested by the O(3)–Ag(2)–O(4) at 129.69(6), O(4)–Ag(2)–O(5) at 107.77(7) and O(3)–Ag(2)–O(5) at 122.20(8)° bond angles, respectively. The shorter distance is between Ag(2)–O(3)

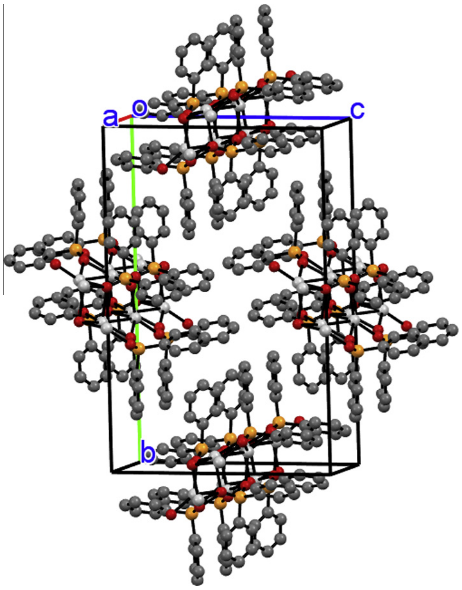


Fig. 7. Packing diagram of complex **2** seen along the *bc* plane.

and Ag(2)–O(4) atoms at equidistant bond lengths of 2.2472(19) and 2.2475(18) Å, respectively. The bond lengths here are clearly influenced by the presence of the triflate ion interacting with the Ag atom, presumably drawing positive charge away from the Ag atom. It is worthy to note that the P(1)–O(1), P(2)–O(2), P(4)–O(4) P(3)–O(3) bond lengths all fall within a narrow range of between 1.507 and 1.511 Å, which is longer than the free ligand at 1.49 Å, but not to the extent that it can fully account for the Ag–O bond length differences. The shortest Ag–O bond lengths are found for Ag(1)–O(1) and Ag(1)–O(2) at distances of 2.0900(18) and 2.101(2) Å, respectively. This short distance presumably arises from a significant positive charge located on the silver atom, capable of drawing the lone pair electrons on the O atoms very close and increasing the bond strength. The atoms O(2)–Ag(1)–O(1) adopts an almost linear geometry with a bond angle of 179.56(7)°. The molecular structure of complex **1** is shown in Fig. 3. The two silver units that make up the dinuclear molecule sit at approximate right angles to each other, as shown in the packing diagram in Fig. 4. Selected bond lengths and angles are shown in Table 3.

In addition, there are four N atoms within the complex that are not coordinated. These N donor atoms could further react to potentially form a supramolecular heterometallic system.

3.3. $[Ag_2\{(\mu\text{-}O)OPPh_2\}\{O_2PPh_2\}]$, (**2**)

The reaction between t-butylamine, DMAP, triethylamine and chlorodiphenylphosphine, in an attempt to form an aminophosphinate led instead to further oxidation yielding a diphenylphosphinic acid ligand. Further reaction with $Ag(SO_3CF_3)$ (molar ratio 1:1) in THF led to the formation of a novel coordination polymer of silver(I) with bridging (μ-O) and non-bridging O atoms, $[Ag_2\{(\mu\text{-}O)OPPh_2\}\{O_2PPh_2\}]$, (**2**), as shown in Scheme 1. An after-the-fact investigation showed that synthesis of pure diphenylphosphinic acid independently, and subsequent reaction with $Ag(SO_3CF_3)$ also leads to complex **2**, as confirmed by ^{31}P NMR analysis. The solution structure of **2**, based on the ^{31}P NMR spectrum, showed a single peak at 33.26 ppm suggesting a fully oxidized 4-coordinate P atom, thus negating any possible M–P bonding. The infrared spectrum of complex **2** showed distinct bands at 3077 and 1175 cm^{-1} assigned to ν(M–O) and ν(P–O) stretching vibrations, respectively.

In the solid-state, complex **2** crystallized in the monoclinic space group $P2_1/c$. Complex **2** is a coordination polymer showing argentophilic Ag(I)···Ag(I) interactions as well as a combination of dative- and covalent bonding to four adjacent oxygen atoms.

Table 5
Crystal data and structure refinement of **L1** and complexes **1** and **2**.

	L1	**1**	**2**
Empirical formula	$C_{16}H_{20}NOP$	$C_{66}H_{76}Ag_2F_6N_4O_{10}P_4S_2$	$C_{24}H_{20}Ag_2O_4P_2$
Formula weight	273.30	1603.05	650.08
T (K)	173(2)	173(2)	150
λ (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	Cc	$P21/c$
a (Å)	9.9212(2)	17.8630(3)	5.8703(2)
b (Å)	10.9651(2)	22.8841(4)	23.9827(7)
c (Å)	13.9669(3)	17.3304(3)	15.6932(5)
α (°)	89.3440(10)	90	90
β (°)	82.3230(10)	94.7690(10)	92.9530(10)
γ (°)	83.0590(10)	90	90
V (Å^3)	1494.75(5)	7059.8(2)	2206.44(12)
Z	4	4	4
Density (calculated) (Mg/m^3)	1.214	1.508	1.957
Absorption coefficient (mm^{-1})	0.176	0.779	1.950
F(000)	584	3280.0	1280
Crystal size (mm^3)	0.27 × 0.25 × 0.21	0.35 × 0.34 × 0.22	0.050 × 0.050 × 0.110
Theta range for data collection	1.87° to 28.31°	1.78° to 28.29°	1.55° to 28.70°
Index ranges	$-13 \leqslant h \leqslant 13$, $-13 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 18$	$-23 \leqslant h \leqslant 23$, $-28 \leqslant k \leqslant 30$, $-23 \leqslant l \leqslant 23$	$-7 \leqslant h \leqslant 7$, $-29 \leqslant k \leqslant 32$, $-21 \leqslant l \leqslant 21$
Reflections collected	47,775	84,418	24,811
Independent reflections (R_{int})	7384 (0.0189)	17,258 (0.0238)	5688 (0.0256)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7384/0/349	17,258/2/860	5688/0/289
Goodness-of-fit (GOF) on F^2	1.040	1.039	1.928
Final R indices [I > 2σ(I)]	R_1 = 0.0331, wR_2 = 0.0856	R_1 = 0.0277, wR_2 = 0.0839	R_1 = 0.0228, wR_2 = 0.0458
R indices (all data)	R_1 = 0.0388, wR_2 = 0.0895	$R1$ = 0.0288, wR_2 = 0.0850	$R1$ = 0.0277, wR_2 = 0.0463
Largest difference peak and hole (e Å^{-3})	0.633 and −0.741	0.997 and −0.606	0.573 and −0.640

The ligand have two binding modes through the O atoms, namely (i) one oxygen atom binding to two silver(I) atoms and the other bridging oxygen binding to a silver(I) atom of the next unit, and (ii) the alternate ligand binds two oxygen atoms to two silver(I) atoms. A portion of the molecular structure within the asymmetric unit is shown in Fig. 5.

The two distinct coordination modes within the complex can be described as trimetallic triconnective and tetrametallic tetraconnective. The former ligand has two distinct oxygen binding modes, namely κO and κ^2O. This resulted in the non-symmetric coordination mode observed, as seen in the elongated bond lengths of P-κ^2O compared to P-κ^1O. For the latter ligand, a symmetric κ^2O bonding is observed, shown by the equivalent bond lengths of P(2)–O(3) and P(2)–O(4) at 1.5144(13) and 1.5178(13) Å, respectively, see Fig. 5. The bond distance between P–O atoms suggests delocalization between the O–P–O atoms because they are intermediate between double- and single P–O bonds, ie P(1)–O(1) and P(1)–O(2) has distances of 1.4982(13) and 1.5120(13) Å, respectively, see Table 4. The geometry around each P atom is slightly distorted tetrahedral as observed from the bond angles O(3)–P(2)–O(4) and O(1)–P(1)–O(2) at 115.90(7)° and 118.25(8)°, respectively. The different bond lengths for Ag(1)–O(3), Ag(2)–O(4), Ag(1)–O(2) and Ag(2)–O(2) from the phosphinic moiety, measuring 2.5134(13), 2.3349(13), 2.2274(13), 2.3962(13) Å, respectively, impacts on the geometry around the Ag atoms which presumably leads to a coordination polymer containing both bridging and non-bridging O atoms, see Fig. 6 and Fig. 7, showing portions of the crystal structure along different axes and planes. Both Ag atoms are surrounded by O-donor atoms in a (pseudo) 4-coordinate arrangement. The argentophilic Ag(1)···Ag(2) interaction is at a bond distance of 3.1596(2) Å.

4. Conclusions

This study reports on a new polymorphic form for the ligand $Ph_2P(O)N(H)CMe_3$, showing a dimeric association in the solid-state as a result of hydrogen bonding. Treatment of the ligand with solid $AgSO_3CF_3$ formed a rare cationic dinuclear silver(I) complex of the type $[Ag(CF_3SO_3)\{OPPh_2N(H)CMe_3\}_2\{Ag(OPPh_2N(H)CMe_3)_2\}]SO_3CF_3$, which contains a short ligand unsupported Ag···Ag interaction binding through two P═O oxygen donor atoms rather than any of the available N donor atoms. The two silver atoms have different geometries caused by a triflate interaction with one silver atom. Further oxidation of the ligand led to diphenylphosphinic acid, which upon reaction with $AgSO_3CF_3$ led to an unusual Ag(I) coordination polymer, $[Ag_2\{(\mu\text{-O})OPPh_2\}\{O_2PPh_2\}]_n$ consisting of O-donor atoms in a 4-coordinate arrangement around the Ag(I) center.

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Appendix A. Supplementary Data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary material under deposition nos. CCDC 1060026, 1060027 & 1060029. Copies of this material can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK Fax: +44(1233)336 033, email deposit@ccdc.cam.ac.uk or CCDC via www.ccdc.cam.ac.uk/data-request/cif.

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