Trinuclear Mixed-valent Gold Complexes Derived from 2-$C_6F_4PPh_2$: Phosphine Oxide Complexes of Gold(III) and an *ortho*-Metallated Complex of Gold(I)

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Crystals of two mixed-valent gold complexes $[(O_2NO)Au^I(\mu\text{-}2\text{-}C_6F_4PPh_2)Au^{III}\{\kappa^2\text{-}2\text{-}C_6F_4P(O)Ph_2\}(\mu\text{-}2\text{-}C_6F_4PPh_2)Au^I(ONO_2)]$ (**14**) and $[(O_2NO)Au^I(\mu\text{-}2\text{-}C_6F_4PPh_2)Au^{III}\{\kappa^3\text{-}2\text{-}C_6F_4P(O)Ph(C_6H_4)\}(\mu\text{-}2\text{-}C_6F_4PPh_2)Au^I]$ (**15**) have been obtained from the reaction of the digold(I,III) complex $[ClAu^I(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)Au^{III}Cl]$ (**5**) with, respectively, a small and a large excess of silver nitrate. Both complexes contain three, approximately collinear metal atoms, the central gold(III) atom being planar-coordinated by a chelate (*O*,*C*)-phosphine oxide formed by oxidation of 2-$C_6F_4PPh_2$ and the carbon atoms of two bridging 2-$C_6F_4PPh_2$ groups. In **14** each of the terminal gold(I) atoms is coordinated by a monodentate nitrate ion and the phosphorus atom of μ-2-$C_6F_4PPh_2$, whereas in **15** the nitrate ion on one of the gold(I) atoms of **14** has been replaced by the carbon atom of a bridging C_6H_4 group derived by Ag^+-promoted cyclometallation of a phenyl group on the neighbouring phosphine oxide.

Key words: Gold, Trinuclear, Cyclometallation, Phosphine Oxide

Introduction

We have recently extended our studies of the chemistry of *ortho*-metallated (cycloaurated) complexes of the type $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ [1, 2] and its methyl-substituted analogues $[Au_2(\mu\text{-}C_6H_3\text{-}n\text{-}Me\text{-}2\text{-}PPh_2)_2]$ (n = 5, 6) [3], to the tetrafluoro species $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **1** [4]. The latter undergoes oxidative addition of halogen atoms to form metal-metal bonded digold(II) complexes $[Au_2X_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ (X = Cl **2**, Br **3**, I **4**), which rearrange on heating to give dihalodigold(I,III) complexes $[XAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuX]$ (X = Cl **5**, Br **6**, I **7**) (Scheme 1). The corresponding bis(oxyanion) complexes in both series, $[Au_2Y_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ (Y = OAc **8**, ONO_2 **9**, OBz **10**) and $[YAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuY]$ (Y = OAc **11**, ONO_2 **12**, OBz **13**) can be prepared from the dihalides by reaction with the appropriate silver salts, although the bis(oxyanion)digold(II) complexes do not isomerise to their digold(I,III) counterparts on heating.

While working with the bis(nitrato)digold(I,III) complex **12**, we isolated and structurally characterised two trinuclear gold complexes in which part of the phosphine unit had been oxidised to a coordinated phosphine oxide. The results are reported in this paper.

Results

Treatment of the colourless dichlorodigold(I,III) complex $[XAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuX]$ (X = Cl) (**5**) with a slight molar excess of silver nitrate gave the corresponding bis(nitrato) complex (X = ONO_2) **12** as a pale yellow solid. The ^{31}P NMR spectrum of **12** showed a pair of singlets at δ = 36.0 and −45.0, assigned to the phosphorus atoms in the

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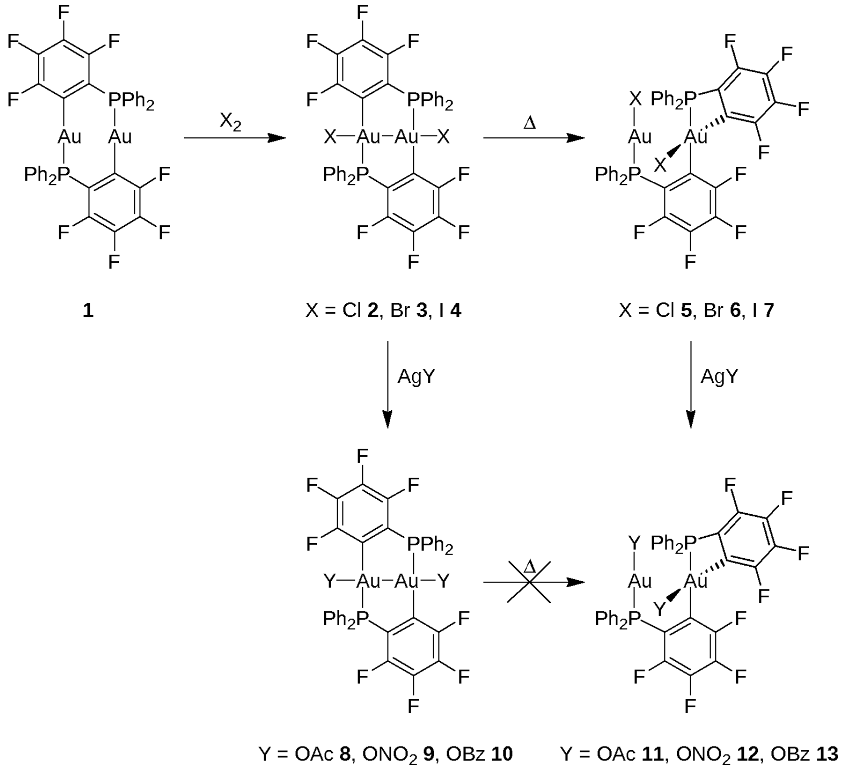

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X = Cl **2**, Br **3**, I **4**

X = Cl **5**, Br **6**, I **7**

Y = OAc **8**, ONO_2 **9**, OBz **10**

Y = OAc **11**, ONO_2 **12**, OBz **13**

Scheme 1.

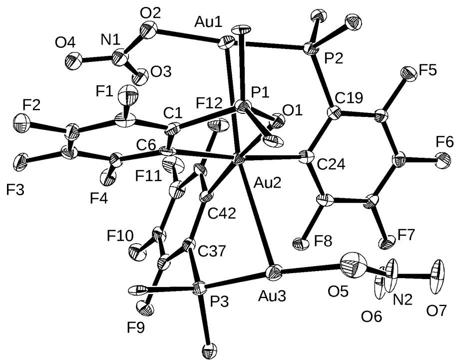

Fig. 1. Molecular structure of one of the two crystallographically independent molecules of the trinuclear gold complex **14** (partially occupied chloro analogue and solvent molecules not shown). Ellipsoids show 30 % probability levels, and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms are shown. The anion positions at Au1 and Au3 are occupied partly by nitrate (s. o. f. 0.71 and 0.75, respectively) and partly by chloride (s. o. f. 0.29 and 0.25, respectively).

Table 1. Selected bond lengths (Å) and angles (deg) for **14**, with estimated standard deviations in parentheses.

Distances			
Au(1)–Au(2)	3.0506(6)	Au(2)–Au(3)	3.1818(7)
Au(1)–O(2)	2.056(11)	Au(1)–P(2)	2.225(3)
Au(2)–O(1)	2.111(7)	Au(2)–C(6)	2.110(12)
Au(2)–C(24)	2.084(12)	Au(2)–C(42)	2.017(11)
Au(3)–O(5)	2.091(14)	Au(3)–P(3)	2.219(3)
P(1)–O(1)	1.519(8)		
Angles			
Au(1)–Au(2)–Au(3)	163.41(2)		
O(2)–Au(1)–P(2)	173.4(4)	O(5)–Au(3)–P(3)	172.4(6)
C(6)–Au(2)–C(24)	173.7(4)	O(1)–Au(2)–C(42)	175.7(4)

bridging and chelating ligands, respectively, and the structure has been confirmed by X-ray diffraction of crystals obtained by slow diffusion of hexane into a CH_2Cl_2 solution (monoclinic, space group $P2_1/c$) [4]. In contrast, crystallisation over a period of 3 d from a solution of CH_2Cl_2/MeOH, which appeared from its initial ^{31}P NMR spectrum to contain pure **12**, gave colourless, triclinic blocks (space group $P\bar{1}$) of a trinuclear species **14** whose structure, with atom labelling, is shown in Fig. 1; selected bond lengths and angles are listed in Table 1.

The three gold atoms of **14** are arranged almost linearly, the Au(1)–Au(2)–Au(3) angle being 163°. The terminal gold atoms, Au(1) and Au(3), are each coordinated, approximately linearly, by a monodentate nitrato group and the phosphorus atom of a bridging $C_6F_4PPh_2$ ligand; these gold atoms are clearly univalent. The carbon atoms of the two bridging carbanions are bound in a mutually *cis*-arrangement to the central gold atom, Au(2), to which is also attached a chelate (*O*,*C*)-2-$C_6F_4P(O)Ph_2$ ligand, evidently derived by oxidation of 2-$C_6F_4PPh_2$. Since Au(2) is attached to three fluoroaryl carbanions and the oxygen atom of the phosphine oxide (phosphanyl group), it is formally trivalent, and, as expected, the coordination geometry about Au(2) is close to square planar.

The nitrato groups at both sites of one of the two independent molecules in the unit cell of **14** are partially replaced by chloride, the NO_3^- to Cl^- ratio being about 3 : 1. In the second independent molecule, only one of the nitrate sites shows similar partial occupancy, while the remaining nitrato ligand shows a two-fold disorder corresponding to the disorder of a neighbouring dichloromethane of solvation.

The separations between the gold atoms in **14** [3.0506(6) and 3.1818(7) Å] are slightly greater than that in **12** [3.0426(4) Å], and fall in the expected range for weak aurophilic interactions [5]. The Au–C bond lengths in the mutually *trans* Au–C_6F_4 units at the central gold(III) atom [2.084(12) and 2.110(12) Å] appear longer than those in Au^{III}-C_6F_5 complexes such as $[Au(C_6F_5)_2(tht)_2][Au(C_6F_5)_4]$ [2.066(6) Å (cation), 2.051(6) – 2.065(6) Å (anion)] [6] and [PPN]-$[Au(C_6F_5)_4]$ [2.054(7) – 2.058(7) Å] [7, 8]; however, within the limits of standard error these differences are only marginal. The length of the Au–C bond *trans* to the oxygen atom of 2-$C_6F_4P(O)Ph_2$ [2.017(11) Å] is significantly shorter than those *trans* to carbon, consistent with the weaker *trans*-influence of neutral oxygen donor ligands [9]. A similar, though somewhat smaller, difference in the Au–C distances in planar pentafluorophenylgold(III) complexes is evident in $[AuCl(C_6F_5)_3]^-$ [10, 11], $[Au(C_6F_5)_3L]$ (L = 4-ferrocenylpyridine) [12] and *cis*-$[Au(C_6F_5)_2(2\text{-}Ph_2PC_6H_4NH_2)]^+$ [13]. The Au–P [2.225(3) and 2.219(3) Å] and Au–O [2.056(11) and 2.091(14) Å] bond lengths in the terminal P–Au–ONO_2 fragments are comparable with those observed in $[Au(ONO_2)(PPh_3)]$ [2.208(3) and 2.074(8) Å, respectively] [14]; the Au–O and P=O bond lengths for the phosphine oxide ligand, 2.111(7) and 1.538(3) Å, respectively, are close to the corresponding values in the recently reported cycloaurated phosphine oxide complex $[AuCl_2\{2\text{-}C_6H_4P(O)(Ph)(N\textit{i}Pr_2)\}]$ [2.009(4) and 1.552(5) Å] [15].

Table 2. Selected bond lengths (Å) and angles (deg) for **15**, with estimated standard deviations in parentheses.

Distances			
Au(1)–Au(2)	3.0649(2)	Au(2)–Au(3)	3.0776(3)
Au(1)–O(2)	2.085(6)	Au(1)–P(1)	2.2239(12)
Au(2)–O(1)	2.088(3)	Au(2)–C(6)	2.071(4)
Au(2)–C(24)	2.083(4)	Au(2)–C(42)	2.009(4)
Au(3)–C(22)	2.054(4)	Au(3)–P(3)	2.0376(12)
P(2)–O(1)	1.538(3)		
Angles			
Au(1)–Au(2)–Au(3)	152.056(7)		
O(2)–Au(1)–P(1)	168.23(15)	P(3)–Au(3) –C(32)	170.84(13)
C(6)–Au(2)–C(24)	173.43(16)	C(42)–Au(2)–O(1)	173.62(15)

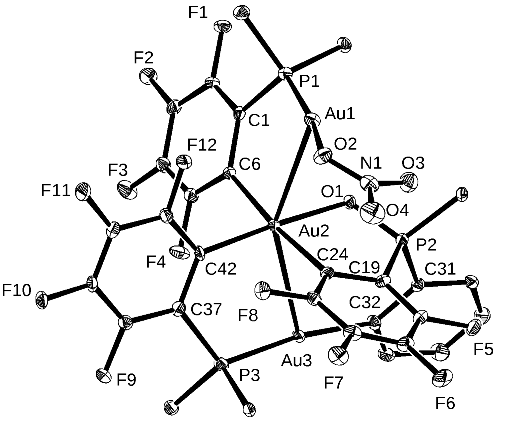

Fig. 2. Molecular structure of the trinuclear gold complex **15** (partially occupied silver/chloro analogue not shown). Ellipsoids show 30 % probability levels, and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the non-metallated phenyl groups attached to the phosphorus atoms are shown. As in compound **14** the nitrate position suffers disorder with alternative chloride occupancy (Cl s. o. f. 0.22), and position Au3 is partially occupied by Au and Ag (s. o. f. 0.58 and 0.42, respectively).

In an attempt to obtain a chloride-free sample of the nitrato complex **14**, we treated the dichlorodigold(II) complex **5** with a tenfold excess of silver nitrate. The main product (*ca.* 90 %) was the bis(nitrato) complex **12**, as judged from the ^{31}P NMR spectrum. However, a number of other peaks of low intensity were also present, including a singlet at δ = 51.6, which may be due to coordinated phosphine oxide. Attempts to separate the components of the mixture by fractional crystallisation failed, but colourless crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/MeOH. Like **14**, the small needle selected was triclinic (space group $P\bar{1}$), but it had different cell dimensions. The structure of this second species, **15**, is shown in Fig. 2 with atom labelling; selected bond lengths and angles are listed in Table 2.

Although **15** resembles **14** in containing three, approximately collinear gold atoms and two bridging 2-$C_6F_4PPh_2$ groups, only one of the terminal gold(I) atoms, Au(1), is coordinated by nitrate. The coordination sphere of the central, trivalent gold atom, Au(2), resembles that of Au(2) in **14**: it comprises the *ortho*-carbon atoms of two mutually *cis* 2-$C_6F_4PPh_2$ groups and the oxygen and carbon atoms of a chelate phosphine oxide ligand, 2-$C_6F_4P(O)(2\text{-}C_6H_4)(Ph)$, which is derived from 2-$C_6F_4P(O)Ph_2$ by orthometallation of one of the P-Ph groups. The metal-carbon bond is formed to the remaining terminal gold atom, Au(3). According to the electron-density map, Au(3) is a site of partial occupancy containing 58 % Au and 42 % Ag; the nitrate site on Au(1) is also partially occupied by chloride (22 %).

In complex **15** the deviation of the three gold atoms from linearity is greater than in **14**, probably because of the geometrical constraint introduced by formation of the additional cyclometallated ring. The separations between the gold atoms [3.0649(2) and 3.0776(3) Å] are similar to those in **14**. The Au–C bond lengths in the mutually *trans* Au-C_6F_4 units in **15** are, on average, slightly less than the corresponding distances in **14** (but within the limits of the standard errors) and, as in **14**, the Au–C distance *trans* to the oxygen atom of the phosphine oxide is significantly less than those *trans* to carbon. The Au–P and Au–O bond lengths in the terminal P–Au–ONO_2 fragment are similar to those in **14**. The Au–C bond length for the metallated phenylene ring [2.054(4) Å] and the Au–P bond length *trans* to the bound carbon atom [2.3076(12) Å] are similar to the corresponding distances in arylgold(I) tertiary phosphine complexes, *e. g.*, [AuPh(PPh_3)] [2.045(6) and 2.296(2) Å, respectively] [16] and [$Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2$] [2.056(3) and 2.300(1) Å, respectively] [1a].

Discussion

At this stage, complexes **14** and **15** have been obtained only in amounts sufficient for characterisation by X-ray crystallography, and efforts are being made to obtain them in larger quantities in order to obtain analytical and spectroscopic data. Clearly, the existence of these novel species would not even have been suspected without the application of X-ray crystallography.

Complexes **14** and **15** join a large family of neutral, cationic and anionic complexes in which three or more gold atoms are held together by bridging ligands, commonly tridentate tertiary phosphines such as $R_2PCH_2P(R)CH_2PR_2$ (R = Me, Ph) or bis(ylides) such as $Ph_2P(CH_2)_2$ [17–21]. They display several points of interest. First, tertiary phosphine oxide coordination is not common in gold chemistry, the first structurally authenticated example having been reported only recently [15]; the only other examples to our knowledge are [$Au^{III}(C_6F_5)_2(OPPh_3)(PPh_3)$]$ClO_4$ [22], [$Au^{III}\{Ph_2P(O)CH_2CH_2P(O)Ph_2\}(PPh_3)$]$ClO_4$ [22] and [$Au^{I}(C_6F_5)(OPPh_3)$] [23]. Second, the unexpected partial replacement of one of the gold atoms in **15** by silver presumably occurs by *trans*-metallation with the large excess of silver nitrate, and is reminiscent of the formation of well-defined, heterobinuclear mesityl and fluoroaryl derivatives containing both metals [24–27]. The observation suggests that it may be possible to prepare 2-$C_6F_4PPh_2$ complexes of silver, and experiments to test this possibility are in progress.

The formation of complex **14**, presumably *via* **12**, is evidently promoted by the presence of nitrate as an oxidising anion, since we have not observed the formation of 2-$C_6F_4P(O)Ph_2$ complexes with the acetato- or benzoato-analogues, **11** and **13**. However, the presence of air may also be important. The uncoordinated PPh_2 group in the complexes [$AuMe_2X$(dppm-κP)] (X = Cl, Br) is oxidised rapidly by air to give the corresponding mono-phosphine oxide complexes [$AuMe_2X$(dppmO-κP)] in some sort of metal-assisted process, even though the P=O group is not coordinated to gold in the final product [28]. Also related to our observations is the reported formation of [Pt(dppmO-$\kappa^2 O,P$)$_2$]$(NO_3)_2$ from a solution containing [$PtCl_2$(dppm)] and silver nitrate in acetone that has been exposed to air [29]. These two reports support the suggestion that the first step in the formation of **14** and **15** is dissociation of a Au–P bond of **12**, but the subsequent steps remain unclear, in particular, how trinuclear species containing $Au^{I}\cdots Au^{III}\cdots Au^{I}$ are formed from the binuclear starting material. A related reduction of a binuclear bis(3,5-dimethylpyrazolato)digold(III) complex successively to trinuclear $Au_2^{III}\cdots Au^{I}$, $Au^{III}\cdots Au_2^{I}$ and Au_3^{I} has been reported recently [30].

Although both spontaneous and Ag^+-promoted cyclometallations that generate five- or six-membered chelate rings *via* C–H bond cleavage are known to occur at gold(III) centres containing N-donor ligands [31], cycloaurated complexes of triarylphosphines are generally accessible only by *trans*-metallation [1–4]. So far as we know, compound **15** is the only example of an aryl(tertiary phosphine)gold(I) complex in which the gold(I)-carbon bond has been formed by cyclometallation; in this case, cyclometallation occurs at a phenyl group on PPh_2 belonging to the 2-$C_6F_4P(O)PPh_2$ ligand attached to the adjacent gold(III) atom. Similar behaviour in a binuclear system has been observed in the reaction of 2-phenylpyridine with $[Re_2Cl_3(PBu_3{}^n)_2]$ to give $[Re_2Cl_3(\mu\text{-}2\text{-}Ph_2PC_5H_4N)\{\mu\text{-}P,C,N\text{-}2\text{-}C_6H_4\text{-}PPh(C_5H_4N)\}]$, in which a PPh_2-derived phenyl group of one of the bridging 2-$Ph_2PC_5H_4N$ ligands has undergone *ortho*-metallation [32].

Experimental Section

Reactions with silver salts were carried out under an atmosphere of dry argon with use of standard Schlenk techniques, although recrystallisations were performed in air; solvents were dried by standard methods. The digold(I,III) complexes $[X\text{Au}(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)\text{Au}X]$ (X = Cl **5**, ONO_2 **12**) were prepared as described previously [4]. ^{31}P NMR spectra were recorded on a Bruker Avance 300 spectrometer and referenced to external 85 % H_3PO_4.

Trinuclear complex 14

A solution of **12** in CH_2Cl_2 was layered with methanol; it was left to stand at room temperature for 3 d, during which time colourless crystals formed. A block crystal was selected, which proved to be **14**.

Trinuclear complex 15

To a solution of **5** in CH_2Cl_2 was added a tenfold excess of silver nitrate, and the mixture was stirred at r. t. for 24 h in the dark. The suspension was filtered through Celite, and the filtrate was layered with methanol. The solution was left to stand at r. t., and after 3 d, colourless crystals had formed. A needle was selected, which proved to be **15**. The ^{31}P NMR spectrum of the crystals, dissolved in C_6D_6, showed peaks at δ = 36.0 and −45.0 due to **12**, together with low-intensity peaks at δ = 0, 20.5, 38.8, 39.7, 51.6, 68.7, and 78.8.

Crystal structure determinations

Crystals suitable for single-crystal X-ray diffraction were obtained by layering a CH_2Cl_2 solution with hexane or methanol. The crystals were mounted on a glass capillary using a drop of inert oil (PARATONE) and transferred to a stream of cold nitrogen. The reflection data were collected on a Nonius Kappa CCD diffractometer equipped with a 95 mm camera and graphite-monochromated MoK_α radiation (λ = 0.71073 Å), in ϕ- and ω-scan modes. Data integration was carried out with the DENZO software [33], and multi-scan absorption correction was performed with the SORTAV program [34]. The crystal structures were solved by Direct Methods using SHELXS-97 [35], or the Patterson method of SHELXS-97. Structure refinement was carried out as a full-matrix least-squares refinement on F^2 using SHELXL-97 [36].

Table 3. Crystal structure data for **14** and **15**.

	14	**15**
Formula	$C_{55}H_{32}Au_3Cl_{2.45}$-$F_{12}N_{1.55}O_{5.65}P_3$	$C_{54.63}H_{30.26}Ag_{0.42}Au_{2.58}$-$Cl_{1.48}F_{12}N_{0.78}O_{3.34}P_3$
M_r	1803.58	1677.83
Crystal size, mm^3	0.18 × 0.18 × 0.06	0.13 × 0.09 × 0.03
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Cryst colour, habit	colourless, block	colourless, needle
a, Å	13.7448(5)	11.6042(3)
b, Å	14.2558(6)	13.1692(3)
c, Å	32.8620(13)	17.8417(3)
α, deg	94.0390(10)	80.6680(10)
β, deg	95.747(2)	79.8200(10)
γ, deg	118.718(2)	80.6780(10)
V, Å^3	5566.6(4)	2623.03(10)
Z	4	2
D_{calc}, g cm^{-3}	2.15	2.12
μ(MoK_α), mm^{-1}	8.2	7.6
F(000), e	3398.8	1583.9
hkl range	$-16 \le h \le 16$	$-16 \le h \le 16$
	$-17 \le k \le 17$	$-17 \le k \le 18$
	$-40 \le l \le 40$	$-24 \le l \le 24$
$((\sin\theta)/\lambda)_{\text{max}}$, Å^{-1}	0.617	0.704
Refl. measured	81884	56598
Refl. unique	21753	15080
R_{int}	0.0993	0.0610
Param. refined	1480	724
$R(F)/wR(F^2)$ [$I \ge 2\sigma(I)$]	0.0628 / 0.1326	0.0374 / 0.0888
$R(F)/wR(F^2)$ (all reflections)	0.0963 / 0.1422	0.0555 / 0.0943
GoF(F^2)	1.078	1.051
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	3.19 / −2.99	2.41 / −2.38

Voids of 37.00 Å^3 were observed in the crystal structure of **15**. They have typically the right size to contain water molecules. It is possible that occluded water molecules were present during crystal growth, but were subsequently removed, leaving these voids intact. No evidence was found for the presence of solvent molecules in these voids. Selected crystal data and details of data collection and structural refinement are listed in Table 3.

CCDC 741929 (**14**), 741930 (**15**) contain 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.

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