Dipyridyl β-diketonate complexes and their use as metalloligands in the formation of mixed-metal coordination networks

Andrew D. Burrows,* Mary F. Mahon,* Catherine L. Renouf, Christopher Richardson, Anna J. Warren and John. E. Warren

Supplementary Information

Experimental details

All starting materials were obtained commercially and used without further purification. Powder diffraction measurements were recorded using a Bruker D8 powder diffractometer, fitted with Goebel mirrors, and using CuK$_\alpha$ radiation of wavelength 1.5414 Å. Samples were placed in 0.3 mm to 0.7 mm diameter Lindemann capillaries, and measured with a 2θ range of 4 - 60°. The step size was 0.02° with time per step of 1.00s. Elemental analyses were conducted by Alan Carver (University of Bath). NMR spectra were recorded at 298 K on a Bruker Avance 300 MHz NMR spectrometer, and referenced to residual *protio* solvent signals for ^{1}H NMR spectra ($CDCl_3$, δ 7.24) and to solvent resonances for $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ 77.2). Mass spectra were recorded on a Bruker MicrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH) coupled to an Agilent 1200 LC system (Agilent Technologies) at the University of Bath or a Voyager-DE-STR MALDI-TOF mass spectrometer at the EPSRC National Mass Spectrometry Service Centre, University of Swansea. The synthesis of dppd and the crystal structure of $[Al(dppd)_3]\cdot 1.25C_7H_8$ are reported in ref. 16.

Synthesis of dmppd

Potassium *tert*-butoxide (2.10 g, 18.7 mmol) was added to a mixture of methyl nicotinate (2.56 g, 18.7 mmol) and 3-acetylpyridine (2.26 g, 18.7 mmol) with gentle warming. After a few minutes the solution solidified. The crude product was taken up in water (50 cm^3) and ethanoic acid added to precipitate a solid, which was washed with water (3 × 10 cm^3) and recrystallised from ethanol-water to give white fluffy solid. Yield 3.26 g (77 %). δ_H (d_6-DMSO): 7.55 (1 H, s), 7.65 (2 H, dd, J = 8.0, 4.8 Hz), 8.53 (2 H, ddd, J = 8.0, 1.8, 1.5 Hz), 8.84 (2 H, dd, J = 4.8, 1.5 Hz), 9.39 (2 H, d, J = 1.8 Hz). The ^{1}H NMR spectrum (Fig. S1) also reveals the presence of the keto tautomer (~7 %).

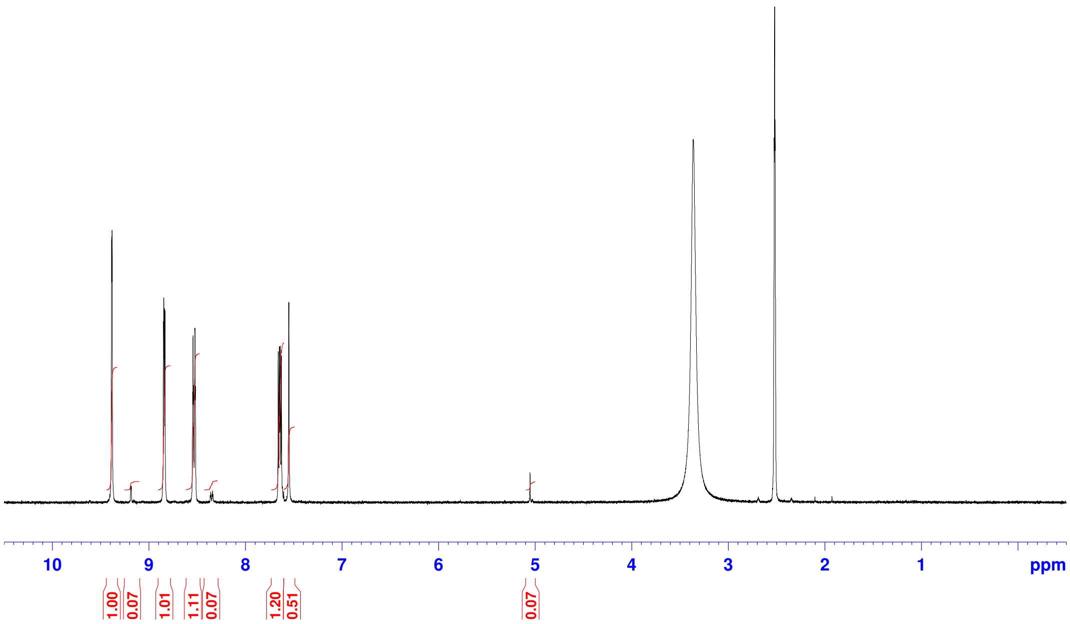

Fig. S1. The ^{1}H NMR spectrum of dmppd in d_6-DMSO.

Synthesis of [Fe(dppd)$_3$] 1

A solution of $Fe(NO_3)_3 \cdot 9H_2O$ (0.646 g, 1.60 mmol) in water (10 cm^3) was added dropwise to a solution of 1,3-di-pyridin-4-yl-propane-1,3-dione (Hdppd) (1.131 g, 5.00 mmol) in water (30 cm^3) containing NaOH (0.216 g, 5.15 mmol). The precipitated material was collected by filtration and washed with water (3 × 10 cm^3). The solid was dissolved in dichloromethane (100 cm^3), and the solution was dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude material recrystallised from dichloromethane-toluene to give red crystals of **1**$\cdot 1.5C_7H_8$. Yield 1.05 g (76%). Found: C, 68.2; H, 4.54; N, 9.81 %. $C_{49.5}H_{39}N_6O_6Fe$ requires C, 68.4; H, 4.52; N, 9.66 %. MS (MALDI) *m/z* 754.1. Calc. for $[C_{39}H_{27}N_6O_6Fe + Na]^+$ *m/z* 754.1.

Synthesis of [Fe(dmppd)$_3$] 2

A solution of Fe(NO$_3$)$_3$·9H$_2$O (0.20 g, 0.50 mmol) in water (4 cm^3) was added dropwise to a solution of 1,3-di-pyridin-3-yl-propane-1,3-dione (Hdmppd) (0.343 g, 1.51 mmol) in 0.1 M aqueous sodium hydroxide (15.5 cm^3, 1.50 mmol). The precipitated material was collected by filtration and washed with water (3 × 10 cm^3). The solid was dissolved in dichloromethane (100 cm^3), and the solution was dried over Na$_2$SO$_4$ and filtered. The solvent was removed under reduced pressure and the crude material recrystallised from dichloromethane-toluene to give red microcrystals of [Fe(dmppd)$_3$]. Yield 0.331 g (91 %). Found: C, 63.8; H, 3.73; N, 11.6 %. $C_{39}H_{27}N_6O_6Fe$ requires C, 64.0; H, 3.72; N, 11.5 %.

Synthesis of [Al(dppd)$_3$] 3

A solution of Al(NO$_3$)$_3$·9H$_2$O (0.60 g, 1.60 mmol) in water (5 cm^3) was added dropwise to a solution of Hdppd (1.131 g, 5.00 mmol) in water (40 cm^3) containing NaOH (0.206 g, 5.15 mmol). The precipitated material was collected by filtration and washed with water (3 × 10 cm^3). The solid was taken up in dichloromethane (100 cm^3) and the solution dried over Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation to *ca.* 20 cm^3. The solution was passed through a short column of alumina eluting with dichloromethane-methanol (98:2) then evaporated and the residue taken up in dichloromethane (20 cm^3) and diluted with toluene (100 cm^3). The colourless crystals of **3**·1.25C_7H_8 that formed overnight were harvested and washed sparingly with fresh toluene. Yield 1.099 g (82 %). Found: C, 70.0; H, 4.59; N, 10.2. $C_{47.75}H_{37}AlN_6O_6$ requires C, 70.1; H, 4.56; N, 10.3 %. δ_H (CDCl$_3$): 6.99 (3 H, s), 7.79 (6 H, dd, *J* = 4.5, 1.6 Hz), 8.75 (6 H, dd, *J* = 4.5, 1.6 Hz). δ_C (CDCl$_3$): 95.34, 121.09, 144.01, 150.67, 184.49. *m/z* (ESI) 703.4 ([M + H]$^+$).

Synthesis of [Al(dmppd)$_3$] 4

A solution of Al(NO$_3$)$_3$·9H$_2$O (0.125 g, 0.33 mmol) in water (2 cm^3) was added to a solution of Hdmppd (0.226 g, 1.0 mmol) in 0.1 M aqueous sodium hydroxide (10 cm^3, 1.0 mmol). The solution was stirred rapidly for 10 min, then the resultant colourless solid was separated by filtration, washed with water (3 × 10 cm^3) and dried at 80 °C. Single crystals of **4**·4CHCl$_3$ were obtained form the slow evaporation of a chloroform solution. Yield 0.18 g (77 %). A sample was heated under reduced pressure for 3 h prior to microanalysis. Found: C, 66.4; H, 3.79; N, 12.2. $C_{39}H_{27}AlN_6O_6$ requires C, 66.7; H, 3.87; N, 12.0 %. δ_H (CDCl$_3$): 6.88 (3 H, s), 7.29 (6 H, dd, *J* = 4.9, 8.0 Hz), 8.19 (6 H, ddd, *J* = 8.0, 1.9. 1.9 Hz), 8.65 (6 H, dd, *J* =

4.9, 1.9 Hz), 9.15 (6 H, d, *J* = 1.9 Hz). δ_H ($CDCl_3$): 94.71, 123.40, 133.00, 135.27, 149.23, 152.79, 183.74. *m/z* (ESI) 725.2 ($[M + Na]^+$).

Synthesis of $[Cu(dppd)_2]$ 5

Hdppd (0.226 g, 1.0 mmol) was dissolved in methanol (5 cm^3) and 1 M aqueous sodium hydroxide (1 cm^3, 1.0 mmol) was added, followed by a solution of $CuCl_2{\cdot}2H_2O$ (0.088 g, 0.50 mmol) in methanol (2.5 cm^3). On addition of the copper(II) solution, a green precipitate formed instantaneously and this was shown by powder X-ray diffraction to be poorly crystalline, even following recrystallisation from hot DMSO-methanol. In order to obtain better quality crystals, Hdppd (0.013 g, 0.059 mmol) was dissolved in DMSO, and 1 M aqueous sodium hydroxide (0.06 cm^3, 0.06 mmol) added. This solution was placed in a vial, and acetonitrile (2 cm^3) was layered carefully on top. Finally, a solution of $CuCl_2{\cdot}2H_2O$ (0.005 g, 0.029 mmol), dissolved in acetonitrile (8 cm^3), was layered carefully on top of this. After 1 week a small quantity of green block-shaped crystals formed at the interface and these were studied by single-crystal X-ray diffraction.

Synthesis of $[Zn(dmppd)_2]$ 6

Al(dmppd) **3** (0.113 g, 0.16 mmol) was dissolved in DMSO (10 cm^3) and added to a solution of zinc(II) acetate hydrate (0.070 g, 0.32 mmol) in methanol (3 cm^3). After 1 week at room temperature, colourless crystals were separated by filtration, and washed with fresh DMSO then methanol. Yield 0.069 g (55 %). The identity of the bulk sample was confirmed by a comparison of the powder X-ray diffraction pattern with that simulated from the single crystal structure (Fig. S2). Found: C, 61.2; H, 3.94; N, 11.0. $C_{26}H_{18}N_4O_4Zn$ requires C, 60.5; H, 3.52; N, 10.9%.

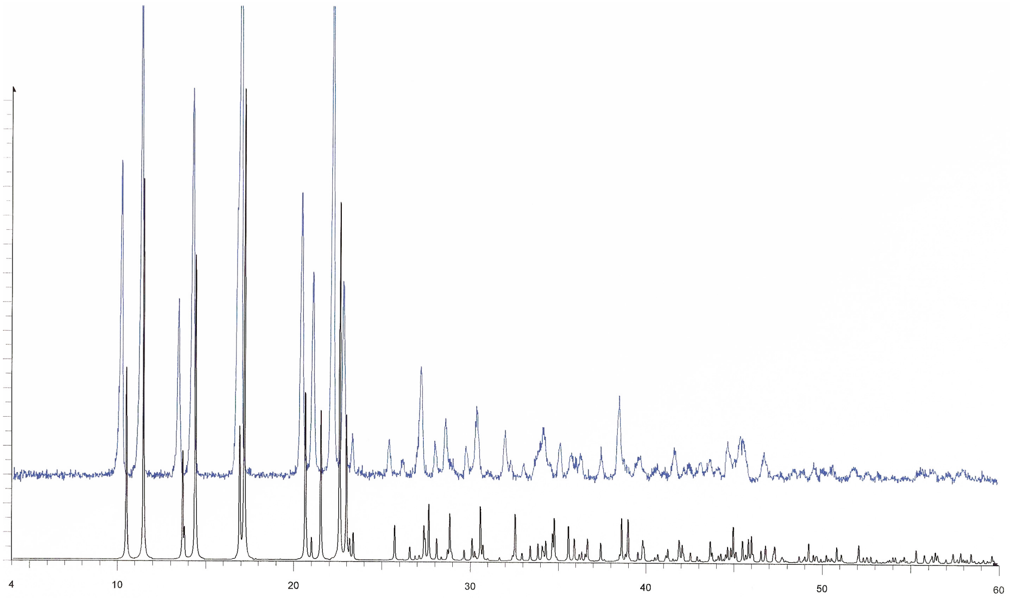

Fig. S2. The X-ray powder diffraction pattern for **6** shown in blue, with the pattern calculated from the crystal structure shown in black for comparison.

Synthesis of $[Eu(dmppd)_2(H_2O)_4]Cl{\cdot}2EtOH{\cdot}0.5H_2O$ 7

Hdmppd (0.2262 g, 1 mmol) was dissolved in warm ethanol (5 cm^3), and a solution of $EuCl_3{\cdot}6H_2O$ (0.0916 g, 0.25 mmol) in ethanol (5 cm^3) was added with stirring. KO^tBu (0.0561 g, 0.5 mmol) was added to the hot solution, and the mixture was allowed to cool slowly to room temperature. Crystals of suitable size for single crystal X-ray analysis formed on cooling, and were separated by filtration. The X-ray powder diffraction pattern revealed that the bulk material contained more than one phase.

Synthesis of $[La(dmppd)_3(H_2O)]{\cdot}2H_2O$ 8

Hdmppd (0.2260 g, 1 mmol) and KO^tBu (0.1131 g, 1 mmol) were heated to reflux in ethanol (10 cm^3) with stirring. A solution of $La(NO_3)_3{\cdot}6H_2O$ (0.1081 g, 0.20 mmol) in water (2 cm^3) was added slowly to the refluxing solution, which was maintained at reflux for 3 hours. The solid product that formed was filtered and washed with water (2 × 3 cm^3). The crude product was dissolved in the minimum amount of ethanol with heating and stirring. The solution was then filtered through a cotton wool plug, and the solvent was allowed to evaporate. Crystals of suitable size for single crystal X-ray analysis were formed. The X-ray powder diffraction pattern revealed that the bulk material contained more than one phase.

Synthesis of $[AgFe(dppd)_3]BF_4 \cdot 2DMSO \cdot 2H_2O$ 9

1$\cdot 1.5C_7H_8$ (0.050 g, 0.057 mmol) was dissolved in DMSO (4 cm^3) and added to a solution of $AgBF_4$ (0.056 g, 0.290 mmol) in DMSO (1 cm^3). The mixture was heated briefly to approximately 60 °C then allowed to stand at room temperature with the vial covered by aluminium foil. Red crystals of **9** formed over a period of 10 h. Found: C, 45.9; H, 3.58; N, 7.50 %. $C_{43}H_{43}AgBF_4FeN_6O_{10}S_2$ requires C, 46.2; H, 3.88; N, 7.51 %. The powder X-ray diffraction pattern for **9** is shown in Fig. S3 in comparison with the pattern simulated from the single crystal structure.

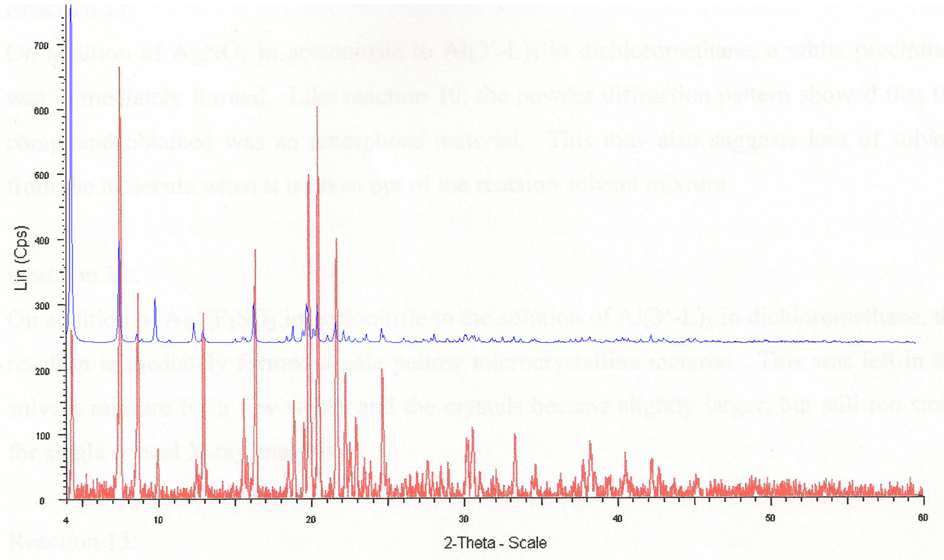

Fig. S3. The X-ray powder diffraction pattern for **9** shown in red, with the pattern calculated from the crystal structure shown in blue for comparison.

Synthesis of $[AgFe(dppd)_3]PF_6 \cdot 3.28DMSO$ 10

1$\cdot 1.5C_7H_8$ (0.050 g, 0.057 mmol) was dissolved in DMSO (4 cm^3) and added to a solution of $AgPF_6$ (0.073 g, 0.290 mmol) in DMSO (1 cm^3). The mixture was heated briefly to approximately 60 °C then allowed to stand at room temperature in a vial covered by aluminium foil. Red crystals of the product formed over a period of 10 h. The material was observed to lose crystallinity rapidly in air, as evidenced by X-ray powder diffraction.

Synthesis of $[AgFe(dppd)_3]SbF_6 \cdot 1.25DMSO$ 11

1$\cdot 1.5C_7H_8$ (0.035 g, 0.04 mmol) was dissolved in DMSO (4 cm^3) and added to a solution of $AgSbF_6$ (0.041 g, 0.12 mmol) in acetonitrile (3 cm^3). The mixture was allowed to stand at room tempearture in a vial covered by aluminium foil. Red crystals of the product formed over several weeks. The material was observed to lose solvent very quickly, resulting in a loss of crystallinity, as evidenced by X-ray powder diffraction.

Synthesis of $[Ag_2Fe(dmppd)_3(ONO_2)]NO_3 \cdot MeCN \cdot CH_2Cl_2$ 12

2 (0.029 g, 0.040 mmol) was dissolved in dichloromethane (3 cm^3) and added to a solution of $AgNO_3$ (0.020 g, 0.12 mmol) in acetonitrile (3 cm^3). The vial was covered with aluminium foil and allowed to stand at room temperature. Red crystals of the product suitable for X-ray analysis were obtained after 1 week. The material was observed to lose solvent very quickly, resulting in a loss of crystallinity, as evidenced by X-ray powder diffraction. Found: C, 41.1; H, 2.62; N, 9.61 %. $C_{39}H_{31}Ag_2FeN_8O_{16} \cdot 4H_2O$ requires C, 41.0; H, 3.09; N, 9.81 %.

Synthesis of $[Ag_2Fe(dmppd)_3(O_2CCF_3)]CF_3CO_2 \cdot 2MeCN \cdot 0.25CH_2Cl_2$ 13

2 (0.029 g, 0.040 mmol) was dissolved in CH_2Cl_2 (3 cm^3) and added to a solution of AgO_2CCF_3 (0.027 g, 0.12 mmol) in acetonitrile (3 cm^3). The vial was covered with aluminium foil and allowed to stand at room temperature. Red microcrystals of the product began to form immediately, and after 1 week some had grown large enough for an X-ray single crystal analysis. The material was observed to lose solvent very quickly, resulting in a loss of crystallinty, as evidenced by X-ray powder diffraction.

X-ray crystallography

The asymmetric unit of **1** consists of one molecule of the iron complex, one full molecule of toluene, and a toluene fragment (half molecule) disordered over two sites, and proximate to an inversion centre. The disorder and symmetry associated with this latter fragment precluded location of the hydrogen atoms therein, and these atoms were omitted from the final least squares refinement.

The asymmetric unit consists of **4** consists of two aluminium complex molecules, in addition to eight molecules of chloroform. The slightly higher than expected *R*1 values reflect the residual electron density maxima in the region of the solvent chlorine atoms, and a fall off of diffracting power of the crystal at Bragg angles greater than 20°.

The chloride ion in **7** was seen to be disordered over two sites in a 60:40 ratio, while the solvent ethanol molecules are presented as fractional molecules (75%, 75% and 50% for the moieties based on O9, O10 and O11 respectively). The solvent portion based on O11 is in the same region of the electron density map as the 40% occupancy chloride. Similarly, the half-occupancy water molecule (O12) shares its region in space with the fractional ethanol molecule based on O10. Oxygen bound hydrogen atoms in the lattice solvent could not be reliably located and hence were omitted from the refinement. Those attached to the ligated waters were located readily however, and refined subject to distance restraints.

The asymmetric unit of **8** contains one lanthanum chelated to three dmppd ligands and one water molecule, plus lattice solvent which was successfully modeled as two water oxygen atoms. This was a very small crystal, and the quality was not ideal, necessitating a data collection time of 38 hours. Water hydrogen atoms could not be reliably located and hence were omitted from the refinement. Similarity restraints were applied to the ADPs for carbons 37-39 during the final least-squares cycles.

In the crystal structure of **9**, the iron and silver atoms are on special positions. The tetrafluoroborate region of the electron density map is subject to substantial smearing. Given that this ion is not present at full occupancy, it is possible that the site is shared with some solvent, but unfortunately this could not be resolved. The structure was refined successfully after accounting for pseudo-merohedral twinning on *c*.

The asymmetric unit for **10** consists of half an iron atom coordinated to one and a half dppd ligands, half a silver atom, half a hexafluorophosphate anion, 0.84 of a DMSO molecule in which the oxygen atom is disordered over two sites, and 0.8 of a DMSO molecule in which the sulfur atom is disordered over two sites. The iron, silver and phosphorus atoms are all located at crystallographic ‘special-positions’. The intensity of the diffraction pattern from the crystal tailed off significantly at higher Bragg angle and hence θ_{max} is somewhat lower than would normally be desirable. Choice of a bigger crystal would not have rectified this situation, and the sample chosen was optimal for this experiment, which may well reflect the disordered nature of the solvent. The difference Fourier map indicated smearing of the electron density in these two regions at a level which could not be more successfully modelled. The alternative space group *Cc* was also considered, but it was clear that this was not an option. The sample also exhibited a small fraction of twinning about *c*. Application of the appropriate twin law served to improve convergence by 0.7%.

Early refinements of the structural model for **11** indicated that there was diffuse electron density in the lattice. Subsequent examination with PLATON showed that this centred on two regions namely in the middle of the *A* and *C* faces of the unit cell. It appeared that these regions contained highly disordered fragments of DMSO but disorder was so extensive that a sensible atomic model could not be developed. Hence the solvent was treated using the SQUEEZE procedure in PLATON. This yielded an estimate of the solvent content (based on the approximate number of electrons contained in the voids) as being in the region of 30 electrons (close to one DMSO molecule). Thus, F(000) and related parameters, as presented, are derived on the basis of inclusion of an additional DMSO molecule in the unit cell.

The anion in **11** (SbF_6^-) is disordered over two sites in a ratio of 55:45. There exists, within each fragment considerable disorder too. Optimum convergence was attained by restraining all Sb–F and F···F distances to being respectively similar. Partial fluorine atoms were treated isotropically. Electron density maxima/minima in the final difference Fourier map are located at chemically insignificant distances from the partial Sb atoms. Indeed, it is highly likely that the partial anions are positionally disordered with fragments of DMSO. Strenuous efforts (>150 runs!) were undertaken in an effort to model such disorder, but the problem could not be satisfactorily resolved – and was hence abandoned. An additional DMSO molecule in the asymmetric unit exhibited 70:30 disorder of the sulfur atom.

The *R*1 value for **12** is higher than desirable as the model had to account for 28% twinning of the crystal about the reciprocal [0 0 1] vector. A smaller crystal size would have helped reduce the residual peaks in the region of the silver atoms, but the benefit would have been outweighed by an earlier tail off in diffraction ability at higher Bragg angles.

The crystals of **13** were small (0.02 × 0.02 × 0.03 mm), and diffraction decreased significantly above 23°. The network voids are filled with two molecules of acetonitrile and a quarter of a dichloromethane molecule per asymmetric unit (proximate to an inversion centre). The residual electron density maximum is in the region of the disordered solvent. Successful refinement was achieved after accounting for 14% pseudo-merohedral twinning along the reciprocal 0 0 1 direction.