

The anionic coordination polymer $\{K_2[Pt_2Ag_8(2,2'\text{-bipyridine})_2(O_2C-CF_3)_{14}]\}_n$

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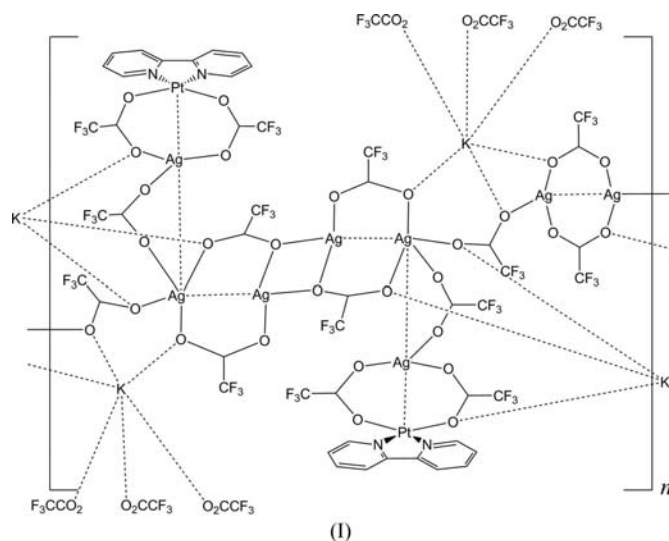
The trimetallic compound *catena*-poly[dipotassium(I) [bis(2,2'-bipyridine)di- μ_3 -trifluoroacetato-dodeca- μ_2 -trifluoroacetato-diplatinum(II)octasilver(I)]], $K_2[Pt_2Ag_8(C_2F_3O_2)_{14}(C_{10}H_8N_2)_2]$, forms an extended structure in the solid state. Electrostatic interactions involving the K^+ ions play a key role in the formation of the extended structure in three dimensions. The Ag^I ions form one-dimensional coordination polymers, with alternating Ag_2 and Ag_6 units linked by $CF_3CO_2^-$ ligands. $Pt \cdots Pt$ interactions perpendicular to the one-dimensional polymerization axis provide another element of long-range order, and electrostatic interactions with K^+ ions provide connectivity between adjacent polymeric structures.

Comment

Coordination polymers are of current interest in materials science due to their potential applications as, for example, luminescent materials (Brandys & Puddephatt, 2001; Shyu *et al.*, 2009), catalysts (Bordoloi *et al.*, 2007) and materials for hydrogen storage (Jeon *et al.*, 2008). Nonetheless, controlling the chemical structure of extended heterometallic networks remains a challenge. Aggregates of $Ag(O_2CR)$ are well documented in the literature and are known to form $[Ag(O_2CR)]_n$ aggregates *via* bridging carboxylate groups (see, for example, Karpova *et al.*, 1999; Zhao *et al.*, 2003; Zhao & Mak, 2005). We have recently reported the synthesis and structural characterization of several bimetallic complexes with the $Ag^I:Pt^{II}$ ratio ranging from 1:1 to 3:1, in which $Pt(2,2'\text{-bipy})$ (2,2'-bipy is 2,2'-bipyridine) acts as a terminator for aggregates of $Ag(O_2CCF_3)$ (Sun *et al.*, 2009). We demonstrated that by controlling the stoichiometry of the reaction between $Pt(2,2'\text{-bipy})(O_2CCF_3)_2$ and $Ag(O_2CCF_3)$, bimetallic structures with well defined geometries may be synthesized reproducibly.

Notably, none of the previously reported $Pt(bipy)\text{-}Ag(O_2CCF_3)$ bimetallic complexes form extended one- or two-dimensional structures *via* the carboxylate bridging ligand

due to the terminating effect of the $Pt(bipy)$ group. Instead, they form one-dimensional extended structures *via* intramolecular $Pt \cdots Pt$ interactions. In addition, despite the use of large excesses of $Ag(O_2CCF_3)$ relative to Pt^{II} , complexes with an $Ag^I:Pt^{II}$ ratio greater than 3:1 were not obtained. We have since discovered the title compound, (I), with the formula



$K_2[Pt_2Ag_8(2,2'\text{-bipy})_2(O_2CCF_3)_{14}]$, obtained serendipitously from the reaction of $Pt(2,2'\text{-bipy})(O_2CCF_3)_2$ with $Ag(O_2C-CF_3)$ in the presence of KCl. We have found that the presence of K^+ ions drastically alters the crystal structure of the coordination polymer, forming structures that are extended in three dimensions as opposed to only one. The repeat unit of (I) is illustrated in the scheme and consists of two asymmetric

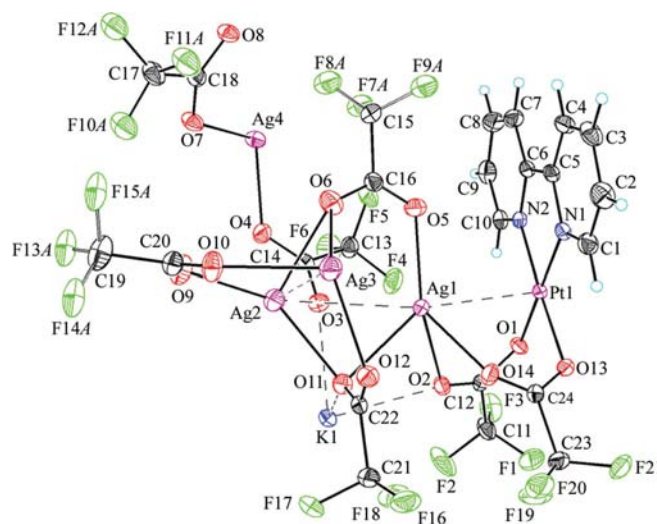
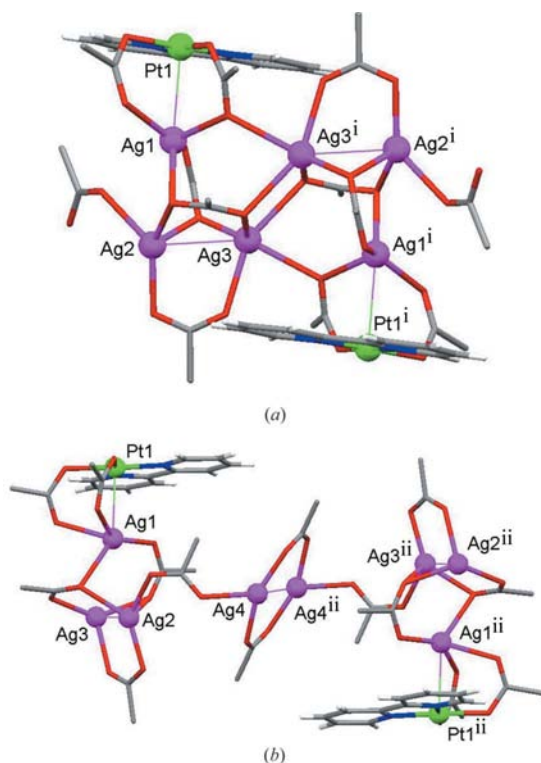


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The minor components of the disordered F atoms have been omitted for clarity.

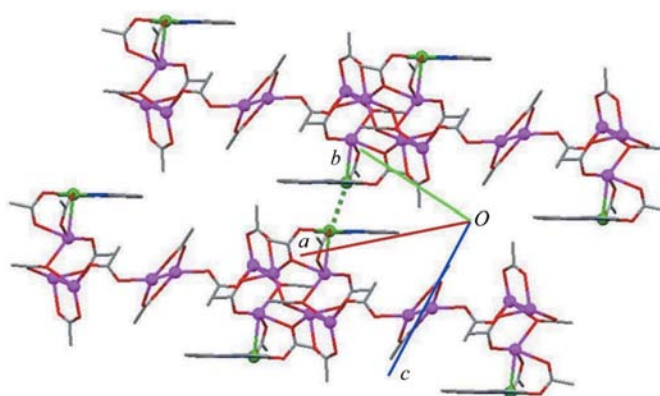
**Figure 2**

(a) The structure of the Pt_2Ag_6 cluster and (b) the $\text{Ag}_2(\text{O}_2\text{CCF}_3)_2$ bridge. F atoms have been omitted for clarity, and Pt and Ag atoms are depicted as small spheres. Thin lines denote intermetallic interactions. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y, -z + 1$.]

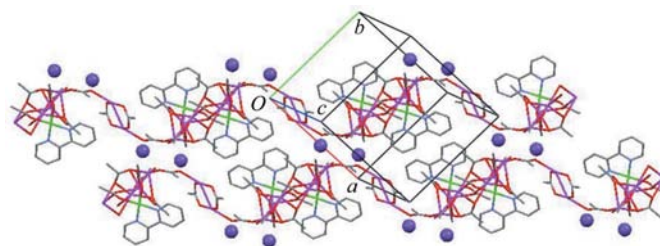
units of $\text{K}[\text{PtAg}_4(\text{bipy})(\text{O}_2\text{CCF}_3)_7]$ related by an inversion centre.

The structure of the asymmetric unit is shown in Fig. 1, where the Pt^{II} centre is in a typical square-planar environment, with normal Pt—O and Pt—N bond lengths. However, the O1—Pt1—O13 and N1—Pt1—N2 angles [83.5 (1) and 81.0 (1)°, respectively] do show significant deviation from an ideal square-planar geometry. The $\text{Ag}4 \cdots \text{Ag}4^{\text{ii}}$ separation of 2.8671 (7) Å [symmetry code: (ii) $-x, -y, -z + 1$] is approximately equal to the $\text{Ag} \cdots \text{Ag}$ distance in metallic silver (2.889 Å; Emsley, 1991), indicative of metal–metal bonding interactions. Meanwhile, the $\text{Ag}1 \cdots \text{Ag}2$ and $\text{Ag}2 \cdots \text{Ag}3$ distances are 3.3140 (5) and 2.9702 (5) Å, respectively, and thus represent only weak interactions between these metal centres. The coordination numbers around the Ag^{I} centres vary considerably, with $\text{Ag}1$ and $\text{Ag}2$ in distorted tetrahedral geometries, $\text{Ag}3$ in a distorted trigonal bipyramidal geometry, and $\text{Ag}4$ adopting a distorted trigonal planar geometry.

In the repeat unit of the $[\text{Pt}_2\text{Ag}_8(2,2'\text{-bipy})_2(\text{O}_2\text{CCF}_3)_{14}]^{2-}$ anion of (I), six Ag^{I} ions and two Pt^{II} ions are joined together by ten carboxylate ligands, as shown in Fig. 2(a). Four of the ten carboxylate ligands adopt a μ_2, η^2 -bridging mode, four adopt a μ_3, η^2 -bridging mode and the remaining two adopt an uncommon μ_4, η^2 -bridging mode. This Pt_2Ag_6 unit is quite different from the neutral $\text{Pt}_2\text{Ag}_6(\text{bipy})_2(\text{O}_2\text{CCF}_3)_{10}$ complex, (II), which we reported earlier (Sun *et al.*, 2009), in terms of the Ag_6 arrangement and carboxylate coordination modes. In (II), four carboxylates act as μ_3, η^2 -bridging ligands, while the

**Figure 3**

The extended structure of (I), showing a $\text{Pt} \cdots \text{Pt}$ interaction. Pt and Ag atoms are depicted as small spheres and F atoms have been omitted for clarity.

**Figure 4**

Packing diagram showing the coordination polymer structure of (I), with K^+ ions shown as small spheres and F atoms omitted.

rest are μ_2, η^2 -type ligands. Interestingly, the Pt_2Ag_6 unit in (I) is further linked to an $\text{Ag}_2(\text{O}_2\text{CCF}_3)_2$ unit *via* a μ_2, η^2 -carboxylate group that binds to $\text{Ag}3$ and $\text{Ag}4'$, forming an extended one-dimensional coordination polymer, as shown in Fig. 2(b). This extra μ_2, η^2 -carboxylate associated with the K^+ cation thus allows the anionic cluster to form extended structures with a Pt:Ag ratio of 1:4.

Neighbouring polymer chains in this system are held together by two distinct interactions. First, chains stack on top of one another *via* attractive $\text{Pt} \cdots \text{Pt}$ interactions, in a similar manner to those observed previously by our group (Sun *et al.*, 2009). The $\text{Pt} \cdots \text{Pt}$ separation in this case is 3.4804 (3) Å, which is typical of previously reported one-dimensional Pt^{II} chains (Du *et al.*, 2008; Wadas *et al.*, 2004). These interactions are shown in Fig. 3. In addition, electrostatic interactions with K^+ ions join adjacent chains together in a direction perpendicular to the (110) plane, as shown in Fig. 4. These K^+ ions are found in a distorted octahedral coordination environment (Fig. 5).

In summary, we have reported a unique $\text{Pt}^{\text{II}}\text{—Ag}^{\text{I}}$ coordination polymer supported by $^-\text{O}_2\text{CCF}_3$ bridging ligands and K^+ ions. We have also demonstrated that the presence of K^+ ions has a significant impact on the formation of $\text{Pt}^{\text{II}}\text{—Ag}^{\text{I}}$ heterometallic complexes. While previously reported complexes of this type form linear chains, the introduction of K^+ causes these compounds to exhibit long-range order in three dimensions. Future avenues for research include the use

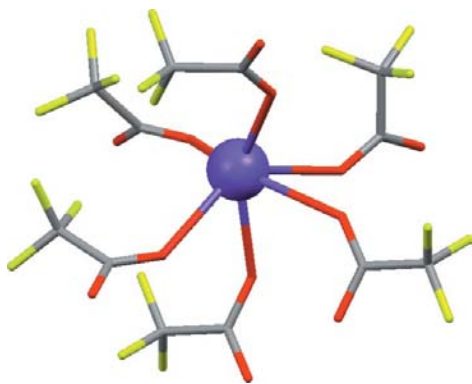


Figure 5
The environment of the K^+ ion, depicted as a sphere. Interactions with six nearby O_2CCF_3 groups are shown.

of alternative cations to synthesize a wider variety of coordination polymers and metal-organic frameworks.

Experimental

$PtCl_2(2,2'$ -bipyridine) (20 mg) was treated with $Ag(O_2CCF_3)$ (42 mg) ($\sim 1:4$ ratio) in the presence of KCl (3.6 mg, ~ 1 equivalent) in CH_2Cl_2 (20 ml). The reaction mixture was stirred for 2 h at room temperature in the dark. After filtration, the yellow solution was concentrated by evaporation to give yellow crystals of (I) as a minor product.

Crystal data

$K_2[Pt_2Ag_8(C_2F_3O_2)_{14}(C_{10}H_8N_2)_2]$	$\gamma = 86.305 (1)^\circ$
$M_r = 3225.98$	$V = 1980.28 (17) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 11.9829 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 12.4737 (6) \text{ \AA}$	$\mu = 5.73 \text{ mm}^{-1}$
$c = 14.4368 (7) \text{ \AA}$	$T = 296 \text{ K}$
$\alpha = 77.378 (1)^\circ$	$0.10 \times 0.10 \times 0.05 \text{ mm}$
$\beta = 70.132 (1)^\circ$	

Data collection

Bruker APEXII CCD area-detector diffractometer	20732 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2008)	7748 independent reflections
$T_{\min} = 0.598$, $T_{\max} = 0.763$	7189 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	112 restraints
$wR(F^2) = 0.058$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\max} = 0.97 \text{ e \AA}^{-3}$
7748 reflections	$\Delta\rho_{\min} = -1.24 \text{ e \AA}^{-3}$
609 parameters	

The disorder associated with atoms F7, F8 and F9 was modelled as two orientations with occupancies which summed to unity of 0.617 (7) and 0.383 (7) for parts *A* and *B*, respectively. Atoms F13, F14 and F15 were modelled similarly, with occupancies of 0.542 (7) and 0.458 (7) for parts *A* and *B*, respectively. Atoms F10, F11 and F12 were modelled as three orientations with occupancies which summed to unity of 0.460 (9), 0.306 (7) and 0.234 (9) for F10/F11/F12 parts *A*, *B* and *C*, respectively. The C—F bond lengths to all components of atoms F10–F15 were restrained to 1.330 (5) \AA to stabilize the refinement, and F atoms from all three disordered $-CF_3$ groups were

Table 1

Selected geometry (\AA , $^\circ$).

$Pt1 \cdots Ag1$	2.9314 (3)	$Ag3 \cdots Ag3^i$	3.7053 (7)
$Ag1 \cdots Ag2$	3.3140 (5)	$Ag4 \cdots Ag4^{ii}$	2.8671 (7)
$Ag2 \cdots Ag3$	2.9702 (5)	$Ag3-O12^i$	2.572 (3)
$Ag3-O6$	2.345 (3)	$K1-O2$	2.771 (3)
$Pt-O1$	2.033 (3)	$K1-O3$	2.717 (3)
$Pt1-O13$	2.038 (3)	$K1-O4^{iii}$	2.923 (4)
$Pt1-N1$	1.981 (3)	$K1-O7^{iii}$	2.738 (3)
$Pt1-N2$	1.985 (3)	$K1-O9^{iii}$	2.745 (4)
$Pt1 \cdots Pt1^{ii}$	3.4804 (3)	$K1-O11$	2.829 (3)
$O1-Pt1-O13$	83.5 (1)	$N1-Pt1-N2$	81.0 (1)
$O1-Pt1-N2$	97.2 (1)	$O13-Pt1-N1$	98.2 (1)
$O2-Ag1-O5$	141.2 (1)	$O2-Ag1-O14$	80.38 (9)
$O5-Ag1-O14$	124.9 (1)	$Pt1-Ag1-Ag2$	167.00 (1)
$Ag1 \cdots Ag2 \cdots Ag3$	76.01 (1)		

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$.

each constrained to have common displacement parameters. $F \cdots F$ distances in these cases were further modelled using distance restraints (*SADI* and *FLAT*; *SHELXL97*; Sheldrick, 2008) as necessary. All H atoms were assigned to geometrically idealized positions, with C—H bond lengths of 0.93 \AA , and were constrained to ride on their parent C atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3165). Services for accessing these data are described at the back of the journal.

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