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Constructing mixed-metal coordination polymers from copper(II)–pyridinedicarboxylate metalloligands

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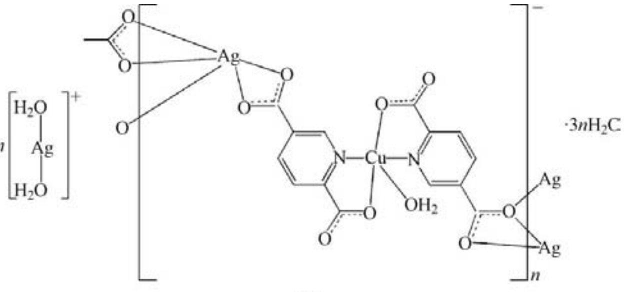
In the mixed-metal complex *catena*-poly[bis[diaquasilver(I)] [bis[aquacopper(II)]-μ_3-pyridine-2,5-dicarboxylato-2′:1:1′κ^5N,O^2:O^5:$O^5,O^{5'}$-μ-pyridine-2,5-dicarboxylato-2:1κ^4N,O^2:$O^5,O^{5'}$-disilver(I)-μ_3-pyridine-2,5-dicarboxylato-1:1′:2″$\kappa^5O^5,O^{5'}$:O^5:N,O^2-μ-pyridine-2,5-dicarboxylato-1′:2‴$\kappa^4O^5,O^{5'}$:N,O^2] hexahydrate], $\{[Ag(H_2O)_2][AgCu(C_7H_3NO_4)_2(H_2O)]\cdot 3H_2O\}_n$, a square-pyramidal Cu^{II} center is coordinated by two N atoms and two O atoms from two pyridine-2,5-dicarboxylate (2,5-pydc) ligands and a water molecule, forming a $[Cu(2,5\text{-pydc})_2(H_2O)]^{2-}$ metalloligand. One Ag^I center is coordinated by five O atoms from three 2,5-pydc ligands and, as a result, the $[Cu(2,5\text{-pydc})_2(H_2O)]^{2-}$ metalloligands act as linkers in a unique μ_3-mode connecting Ag^I centers into a one-dimensional anionic double chain along the [101] direction. The other Ag^I center is coordinated by two water molecules, forming an $[Ag(H_2O)_2]^+$ cation. Four adjacent Ag^I centers are associated by Ag$\cdots$Ag interactions [3.126 (1) and 3.118 (1) Å], producing a Z-shaped Ag_4 unit along the [010] direction and connecting the anionic chains into a two-dimensional layer structure. This study offers information for engineering mixed-metal complexes based on copper(II)–pyridinedicarboxylate metalloligands.

Comment

Coordination polymers constructed from metal ions and bridging ligands have been of great interest owing not only to their structural diversity but also to their many properties, such as host–guest chemistry, porosity, and magnetic, electronic and optical properties (Caneschi *et al.*, 2001; Kitagawa *et al.*, 1999). To date, a large number of monometallic coordination polymers have been prepared by the combination of organic spacers and metal centers (Evans & Lin, 2002; Kitagawa *et al.*, 2004). Compared with monometallic coordination polymers, the design and synthesis of mixed-metal coordination polymers have received less attention (Kahn *et al.*, 1988; Pei *et al.*, 1988). In principle, such heterometallic materials might exhibit interesting physical properties, such as electrical conductivity or magnetic ordering, resulting from interactions between two neighboring metal centers connected by a suitable linker (Dong *et al.*, 2000).

There are basically two approaches to the synthesis of mixed-metal coordination polymers. The one-step approach utilizes multidentate organic ligands to bind two different metal ions in a one-pot reaction. This method has been applied in the syntheses of some 3*d*–4*f* heterometallic compounds (Cheng *et al.*, 2008; Liang *et al.*, 2000; Luo *et al.*, 2007). In the two-step approach, a metalloligand, which acts as a framework linker and a source of one metal, is synthesized first and then the metalloligand is reacted with another metal ion, usually by diffusion or hydrothermally so that the two types of metal centers co-exist in the framework (Chapman *et al.*, 2002; Ciurtin *et al.*, 2002; Noro *et al.*, 2005). Using this approach, Noro *et al.* (2002*a*,*b*) have used a metalloligand, $[Cu(2,4\text{-pydc})_2]^{2-}$ (2,4-H_2pydc is pyridine-2,4-dicarboxylic acid), which was usually obtained as the Et_3NH^+ salt, to prepare mixed-metal coordination polymers . We have developed a simplified two-step method to assemble mixed-metal frameworks by using 2,5-pydc ligands as organic spacers. In our approach, the metalloligand was not isolated in the first step and ammonia was added during the second step to assist in the formation of the mixed-metal complex. We report here the synthesis and structure of a mixed-metal coordination polymer formulated as $\{[Ag(H_2O)_2][AgCu(2,5\text{-pydc})_2(H_2O)]\cdot 3H_2O\}_n$, (I), which exhibits a one-dimensional anionic double chain structure.



(I)

The asymmetric unit of (I) contains one Cu^{II} center, two Ag^I centers, two 2,5-pydc ligands, three coordinated water molecules and three uncoordinated water molecules (Fig. 1). The absence of IR absorption bands around 1700 cm^{-1}, attributed to a protonated carboxylate group, indicates the full deprotonation of the 2,5-pydc ligands. Cu1 is coordinated by two pyridyl N atoms and two 2-carboxylate O atoms from two 2,5-pydc ligands and by one water molecule in a distorted square-pyramidal geometry forming the $[Cu(2,5\text{-pydc})_2(H_2O)]^{2-}$ metalloligand. Cu1 deviates from the basal plane formed by N1, N2, O1 and O5 toward the apical O1*W* atom by 0.1264 (19) Å. The angles at Cu1 between O1*W* and the basal atoms are in the range 91.49 (13)–97.64 (14)°. Ag1 is bonded to three 5-carboxylate O atoms [O7, O3^{i} and O4^{ii}; symmetry codes: (i) $x-1, y, z-1$; (ii) $-x+2, -y+1, -z+1$] from three

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2,5-pydc ligands in a distorted T-shaped geometry, with Ag1—O distances of 2.231 (3), 2.241 (4) and 2.664 (4) Å, respectively (Table 1). The other O atoms of the 5-carboxylate groups (O8 and O4^{i}) also weakly coordinate to Ag1, with longer Ag1—O distances of 2.722 (3) and 2.747 (4) Å. Thus, two [Cu(2,5-pydc)$_2$(H$_2$O)]$^{2-}$ metalloligands bridge two Ag1 centers, forming a cyclic unit. The π–π interactions between the pyridyl groups in this ring have a centroid–centroid distance of 3.773 (3) Å. The Cu$\cdots$Cu distance in the ring is 3.965 (1) Å. These cyclic units are further connected along the [101] direction through Ag$_2$O$_2$ four-membered rings into a one-dimensional anionic double chain (Fig. 2).

Ag2 and two water molecules form an approximately linear cation (Fig. 1). Atoms Ag1 and Ag2, together with their centrosymmetrically related equivalents, form a Z-shaped Ag$_4$ unit through Ag$\cdots$Ag interactions [3.1264 (7) and 3.1177 (8) Å]. According to the literature, Ag$_n$ units have several geometries, including linear (Hou & Li, 2005), annular (Estienne, 1986), polyhedral (Wei *et al.*, 2004; Zhao *et al.*, 2003) and extended chain (Hannon *et al.*, 2002; Sang & Xu, 2006). An Ag$_4$ unit similar to that in (I) has been found in related compounds (Chen & Liu, 2003; Lin *et al.*, 2004). Though argentophilic interactions are weaker than aurophilic interactions, it is thought that argentophilic interactions are similar to O—H$\cdots$O hydrogen bonds in strength (Pyykkö, 1997). Therefore, argentophilic interactions can be used as one of the noncovalent interactions that facilitate the construction of topologically interesting supramolecular systems. In (I), the Ag$_4$ units extending in the [010] direction connect the anionic chains into a two-dimensional layer, as shown in Fig. 3. The layer structure is supported by intralayer hydrogen bonds between the coordinated water molecules and carboxylate O atoms (O2*W*—H2*A*$\cdots$O4^{ii} and O3*W*—H3*B*$\cdots$O7; see Table 2 for details). Interlayer hydrogen bonds involving the coordinated and uncoordinated water molecules and carboxylate O atoms link the layers into a three-dimensional supramolecular structure.

In the [Cu(2,5-pydc)$_2$]$^{2-}$ metalloligand, each 2,5-pydc ligand chelates the Cu^{II} center through the pyridyl N atom and one O atom of the 2-carboxylate group, leaving the other O atom of the 2-carboxylate group and two O atoms of the 5-carboxylate group as donors to the other metal centers. Thus, six possible coordination sites are available for this metalloligand, as shown in Fig. 4. A search of the Cambridge Structural Database (Version 5.29; Allen, 2002) revealed that the [Cu(2,5-pydc)$_2$]$^{2-}$ metalloligand connects metal ions in two types of μ_2-mode, μ_2-(κ^2O^2:O^5) and μ_2-(κ^2O^1:O^5), one μ_4-mode, μ_4-(κ^4O^2:O^3:O^5:O^6), and one μ_6-mode, μ_6-(κ^6O^1:O^2:O^3:O^4:O^5:O^6). It is worthy of note that the metalloligand in (I) connects three Ag^{I} centers through the 2, 3, 5 and 6 sites, exhibiting a unique μ_3-mode, μ_3-(κ^5O^2:O^2,O^3:O^5,O^6) (Fig. 4), which has not been reported previously. Our results indicate that the [Cu(2,5-pydc)$_2$]$^{2-}$ unit can serve as a versatile ligand for the construction of mixed-metal coordination polymers.

In conclusion, we have prepared a mixed-metal complex using a simplified two-step procedure. The [Cu(2,5-pydc)$_2$(H$_2$O)]$^{2-}$ metalloligand acting as a framework linker bridges

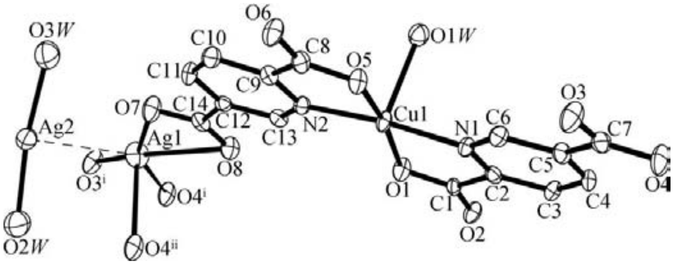

Figure 1
The asymmetric unit of (I), together with symmetry-related atoms to complete the Ag1 coordination. Displacement ellipsoids are drawn at the 50% probability level. H atoms and uncoordinated water molecules have been omitted for clarity. [Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $-x + 2, -y + 1, -z + 1$.]

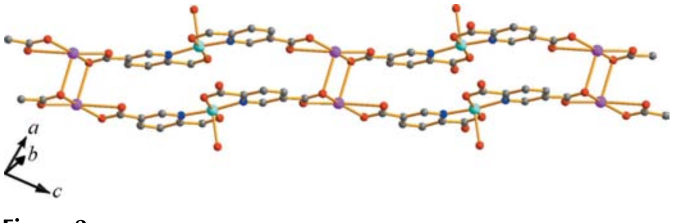

Figure 2
The one-dimensional anionic double chain in (I). H atoms have been omitted for clarity.

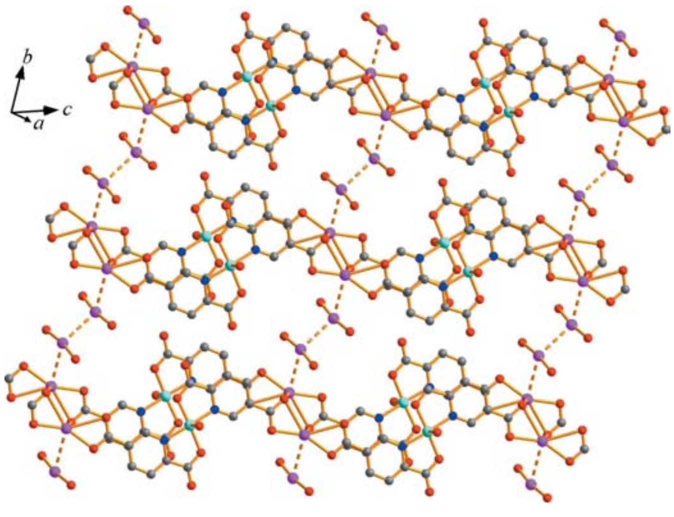

Figure 3
The two-dimensional layer structure in (I). Dashed lines denote Ag$\cdots$Ag interactions.

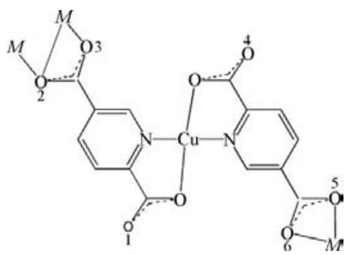

Figure 4
Schematic representation of coordination modes of the [Cu(2,5-pydc)$_2$]$^{2-}$ metalloligand. The six possible coordination sites are numbered and the μ_3-(κ^5O^2:O^2,O^3:O^5,O^6) mode observed in (I) is shown.

the other Ag^I centers, leading to a one-dimensional polymeric chain. This work suggests a new synthetic approach for the preparation of mixed-metal complexes based on a Cu^{II}–pyridinedicarboxylate metalloligand and a second metal ion, which can be extended to other bimetallic complexes.

Experimental

An aqueous solution (20 ml) of $Cu(NO_3)_2\cdot 3H_2O$ (0.125 g, 0.3 mmol) and a suspension of 2,5-H_2pydc (0.083 g, 0.3 mmol) in ethanol (10 ml) was refluxed for 24 h until a clear solution was obtained. To this solution, an aqueous solution (5 ml) of $AgNO_3$ (0.085 g, 0.5 mmol) was added. Aqueous NH_3 (25%, 0.06 ml) was then added slowly to the reaction mixture. The resulting solution was filtered. Blue crystals were obtained by allowing the filtrate to stand at room temperature for several days [yield 0.112 g, 52% (based on Cu)].

Crystal data

$[Ag(H_2O)_2][AgCu(C_7H_3NO_4)_2(H_2O)]\cdot 3H_2O$
$M_r = 717.58$
Triclinic, $P\overline{1}$
$a = 7.4307$ (8) Å
$b = 10.8485$ (11) Å
$c = 13.5487$ (14) Å
$\alpha = 74.685$ (2)°
$\beta = 85.084$ (2)°
$\gamma = 88.818$ (2)°
$V = 1049.52$ (19) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.93$ mm^{-1}
$T = 187$ K
0.26 × 0.17 × 0.04 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.513$, $T_{max} = 0.889$
5691 measured reflections
3822 independent reflections
3113 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$

Table 1
Selected bond lengths (Å).

Cu1—O1	1.951 (3)	Ag1—O4^{i}	2.747 (4)
Cu1—O5	1.966 (3)	Ag1—O7	2.241 (4)
Cu1—N1	1.991 (4)	Ag1—O8	2.722 (3)
Cu1—N2	1.986 (4)	Ag1···Ag2	3.1264 (7)
Cu1—O1*W*	2.298 (4)	Ag2—O2*W*	2.130 (5)
Ag1—O3^{i}	2.231 (3)	Ag2—O3*W*	2.134 (5)
Ag1—O4^{ii}	2.664 (4)	Ag2···Ag2^{iii}	3.1177 (8)

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x+2, -y+1, -z+1$; (iii) $-x+1, -y, -z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···O8^{iv}	0.82 (4)	1.87 (4)	2.684 (5)	172 (5)
O1*W*—H1*B*···O4*W*	0.82 (4)	1.97 (4)	2.739 (5)	157 (5)
O2*W*—H2*A*···O4^{ii}	0.83 (5)	2.11 (5)	2.924 (6)	166 (7)
O2*W*—H2*B*···O1*W*^{v}	0.83 (5)	2.22 (5)	3.046 (6)	172 (6)
O3*W*—H3*A*···O4*W*^{vi}	0.82 (6)	2.34 (5)	3.115 (6)	156 (5)
O3*W*—H3*B*···O7	0.82 (6)	2.20 (5)	2.861 (6)	138 (7)
O4*W*—H4*A*···O5^{vii}	0.82 (3)	2.18 (3)	2.931 (5)	153 (5)
O4*W*—H4*B*···O2^{iv}	0.82 (2)	2.01 (3)	2.770 (5)	154 (5)
O5*W*—H5*A*···O6*W*^{viii}	0.83 (5)	1.89 (5)	2.708 (7)	174 (6)
O5*W*—H5*B*···O3^{vii}	0.82 (4)	1.89 (4)	2.697 (5)	167 (6)
O6*W*—H6*A*···O5*W*^{ix}	0.82 (5)	1.91 (5)	2.708 (6)	165 (6)
O6*W*—H6*B*···O6^{x}	0.82 (2)	1.90 (3)	2.691 (6)	162 (8)

Symmetry codes: (ii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y+1, -z+1$; (v) $x, y, z-1$; (vi) $-x+1, -y, -z+1$; (vii) $x-1, y, z$; (viii) $-x, -y+1, -z+2$; (ix) $x, y+1, z$; (x) $x-1, y+1, z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.097$
$S = 0.99$
3822 reflections
334 parameters
18 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 1.60$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

H atoms on C atoms were positioned geometrically and refined using a riding model [C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. H atoms of water molecules were located in a difference Fourier map and refined with distance restraints of O—H = 0.82 (1) Å and H···H = 1.34 (1) Å, and with $U_{iso}(H) = 1.2U_{eq}(O)$. The highest residual electron density was 0.83 Å from Ag1 and the deepest hole 0.75 Å from Ag1.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); 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: FN3027). Services for accessing these data are described at the back of the journal.

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