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Chains and Nanochannels Self-Assembled from Carbido Clusters, Silver Ions and Heterocyclic Ligands – Crystal Structures of the 1D Coordination Polymers $[\{AgOC_4H_8\{Rh_6C(CO)_{15}\}AgOC_4H_8\}pyz]_\infty$ and $[bipy\{Ag_2Ru_6C(CO)_{16}\}(bipy)_2\{Ag_2Ru_6C(CO)_{16}\}\cdot 2C_4H_8O]_\infty$

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Two prototypical carbido anionic clusters, the prismatic $[Rh_6C(CO)_{15}]^{2-}$ and the octahedral $[Ru_6C(CO)_{16}]^{2-}$, can add two electrophilic Ag–NCMe$^+$ fragments, which were exploited to condense the clusters with bifunctional heterocyclic ligands, such as pyrazine (pyz) or 4,4′-bipyridine (bipy), forming 1D chains of formula $[\{Ag(OC_4H_8)\{Rh_6C(CO)_{15}\}Ag(OC_4H_8)\}pyz]_\infty$ and $[bipy\{Ag_2Ru_6C(CO)_{16}\}(bipy)_2\{Ag_2Ru_6C(CO)_{16}\}\cdot 2C_4H_8O]_\infty$, both characterized by single-crystal X-ray diffraction. In the former, the two Ag$^+$ ions are on opposite sides, and the chains are tightly packed. In the latter, the two silver ions are directly bound, and the metal clusters are connected alternatively by one and two linkers, giving rise to large channels.

Introduction

The field of 1–3D coordination polymers is rapidly expanding, since the resulting materials can find wide applications.[1] Oxido-bridged polymetallic ions are frequently used as connectors, owing to their structural rigidity. These units are sometimes mentioned as clusters,[2] even if no direct bonds exist between the metal atoms. To the contrary, the structures based on "true" metal clusters are less common, the most recent examples being the polymers of $[TeFe_3(CO)_9Cu_2]$,[3] $[Fe_4Cu_2C(CO)_{12}]$[4] and $[(C_5Me_5)_2Mo_2S_4Cu_2]$[5] (formed with bridging bifunctional ligands). Other cluster-derived polymers exploit inorganic ligands {as bridging halides in $[Pt_9(CO)_{18}(CdCl_2)_2]^{2-}$[6] or $[Pd_3(C_7H_7)_2Cl_2]$[7]} metal–metal bonds {as in the superwire $[\{AgRu_6C(CO)_{16}\}^-]_\infty$[8]}, or hydrogen bonds {as found in the arrays of $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters with nicotinamide[9]}.

The carbide clusters $[Rh_6C(CO)_{15}]^{2-}$[10] and $[Ru_6C(CO)_{16}]^{2-}$[11] can add up to two M–L$^+$ fragments, with M = Cu, Ag, Au. Some of these heterometallic neutral adducts are sufficiently robust for the preparation of new coordination polymers, which are described in this communication.

Results and Discussion

In the past, acid–base adducts between anionic carbonyl clusters and electrophilic moieties (especially $[Au\text{–}PR_3]^+$) were used to increase the nuclearity of the clusters.[12] $[Rh_6C(CO)_{15}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$ can also add $[M\text{–}NCMe]^+$ (M = Cu, Ag) fragments,[13–15] and the products can be isolated and characterized by X-ray diffraction. Thus, the salts $(NMe_3CH_2Ph)_2[Rh_6C(CO)_{15}]$ and $(NEt_4)_2[Ru_6C(CO)_{16}]$ were dissolved in THF and treated with $AgBF_4$ in the 1:2 molar ratio in the presence of MeCN. The resulting neutral heterometallic clusters $M_6C(CO)_x(AgNCMe)_2$ (M = Rh, x = 15; M = Ru, x = 16) were identified by IR spectroscopy and purified by precipitation. Concentrated THF solutions of the clusters were then layered with toluene solutions of different bifunctional linear heterocyclic ligands (such as pyrazine and 4,4′-bipyridine), aiming to the self-assembly of infinite chains. The same reactions were performed with $[Cu(NCMe)_4]BF_4$, with identical workup. The materials obtained, insoluble in most organic solvents, were all characterized by elemental analysis and ATR solid-state IR spectroscopy. Only the products containing silver atoms formed single crystals, suitable for X-ray diffraction. By this way, the two polymeric compounds $[\{Ag(OC_4H_8)\{Rh_6C(CO)_{15}\}Ag(OC_4H_8)\}pyz]_\infty$ (**1**)[16] and $[bipy\{Ag_2Ru_6C(CO)_{16}\}(bipy)_2\{Ag_2Ru_6C(CO)_{16}\}\cdot 2C_4H_8O]_\infty$ (**2**)[17] could be identified.

The asymmetric crystallographic units of **1** and **2** (corresponding to the monomers) are shown in Figure 1 and Figure 2, respectively. Since the bridging heterocycles sit on cristallographic inversion centres they appears as split into two halves.

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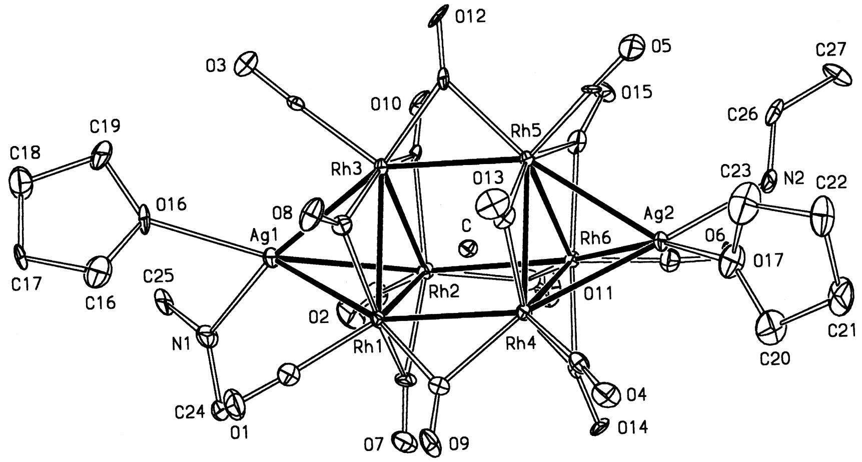

Figure 1. ORTEP drawing of [{Ag(OC$_4$H$_8$){Rh$_6$C(CO)$_{15}$}Ag(OC$_4$H$_8$)}pyz]. The carbon atoms of the carbonyl groups are labelled as the oxygen atoms to which they are attached. Bond-length ranges: Rh–Rh 2.77–2.81, Rh–Ag 2.78–2.88, Rh–C(int) 2.11–2.16 Å.

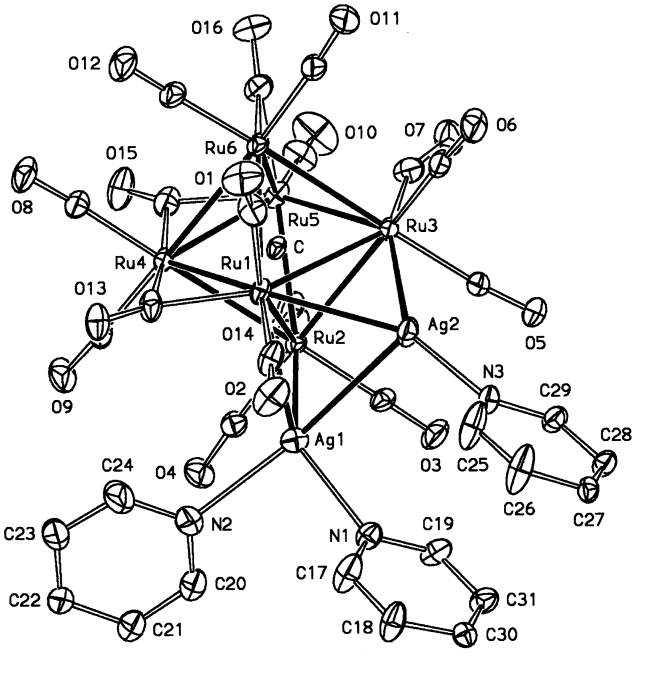

Figure 2. ORTEP drawing of [{Ag$_2$Ru$_6$C(CO)$_{16}$}(bipy)$_{1.5}$]. The carbon atoms of the carbonyl groups are labelled as the oxygen atoms to which they are attached. Bond-length ranges: Ag1–Ag2 2.983(1), Ru–Ru 2.81–3.1, Ru–Ag 2.75–2.85, Ru–C(int) 2.03–2.07, Ag–N 2.21–2.39 Å.

Compound **1** is constituted by trigonal-prismatic rhodium clusters, with two silver ions capping opposite triangular faces. However, in contrast to the structurally characterized molecules [Rh$_6$C(CO)$_{15}$(AgL)$_2$] (L = PPh$_3$, NCMe),[13] the Ag$^+$ sites display a higher coordination number and are coordinated not only by the bridging pyrazine ligand, but also by a THF molecule. The Rh–N and Rh–O geometrical parameters are very similar, and the two different ligands seem to be equally bound to the Ag$^+$ ion. The two THF ligands of the same cluster are on the same side, but are in a pseudo-*trans* relation with those of the next unit (see Figure 3).

In contrast, the two silver atoms found in **2** are directly bound to each other [Ag–Ag 2.983(1) Å], bridging a triangular face in a sort of μ_3:η^2-Ag$_2$ coordination, comparable with that found in [Ru$_6$C(CO)$_{16}$(CuNCMe)$_2$],[14] but different from [Ru$_6$C(CO)$_{16}$(AuPPh$_2$Me)$_2$],[18] in which the two Au–L groups are capping opposite faces. It is worthwhile mentioning that other isomers of the latter compound have been detected by ^{31}P NMR spectroscopy and that also the silver atoms should be potentially able to cap the opposite side of the cluster, as shown by the superwire [{AgRu$_6$C(CO)$_{16}$}$^-$]$_\infty$.[8] The four silver atoms of two Ru$_6$Ag$_2$ clusters are linked by two parallel bipyridine molecules forming a cyclic dimer.

The polymer is formed by connecting these dimers with a third ligand, perpendicular to the others [N1–Ag1–N2 89.5(1)°]. Thus, each cluster in the chain is alternatively separated by one or two linkers, as shown in Figure 4.

This exact arrangement was also found in the polymer [Cu$_2$TeFe$_3$(CO)$_9$(bipy)$_{1.5}$],[3] whith π-stacking giving a substantial contribution to its stability (in **2** the centers of the heterocyclic rings are 3.7 Å apart).

An even more important difference can be seen in Figures 5 and 6, which show the crystal packing of the two materials. In **1**, the clusters are densely packed, and the unit cell appears to be completely filled by two parallel chains.

In contrast, the structure of **2** has large cavities, which are estimated to be 19 × 9 Å.

The solvent molecules do not fill these channels, since the clathrated toluene is adsorbed on the edges, and the THF molecules are intercalated between two clusters and held in place by hydrogen bonds with the carbonyl groups (C–H···OC 2.78–2.85 Å; see Figure S1 in the Supporting Information) contributing to increase the width of the cavities. The elemental analyses are slightly out of limits (C and H low, N high) suggesting that toluene is slowly released and

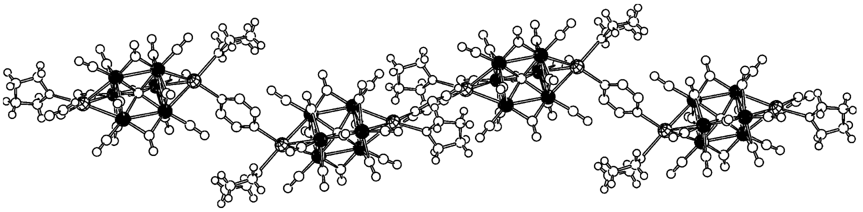

Figure 3. Chain found in **1**.

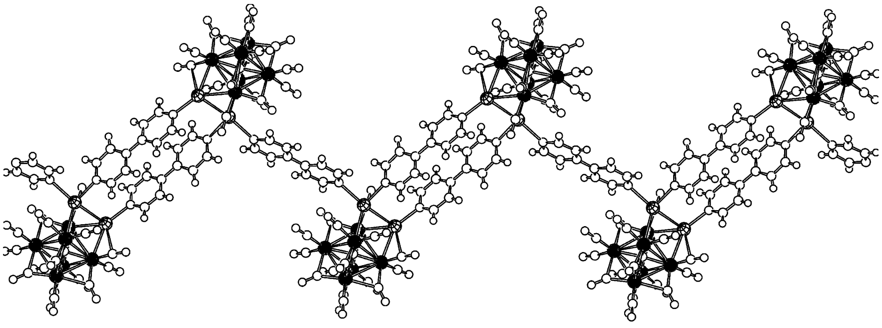

Figure 4. Chain found in **2**, with the clusters being spaced alternatively by one and two bipyridine ligands.

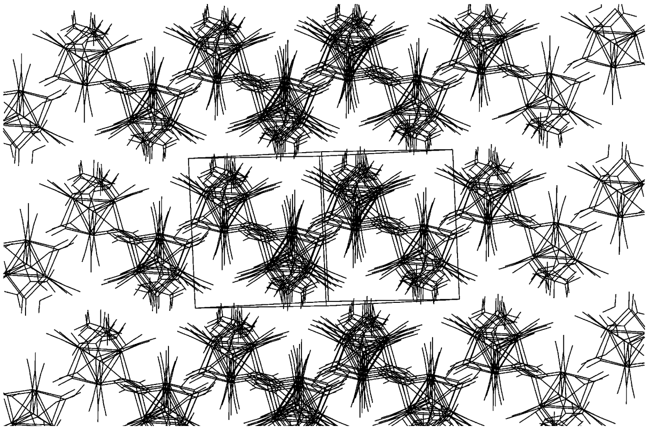

Figure 5. Crystal packing of **1**, viewed along the *B* face.

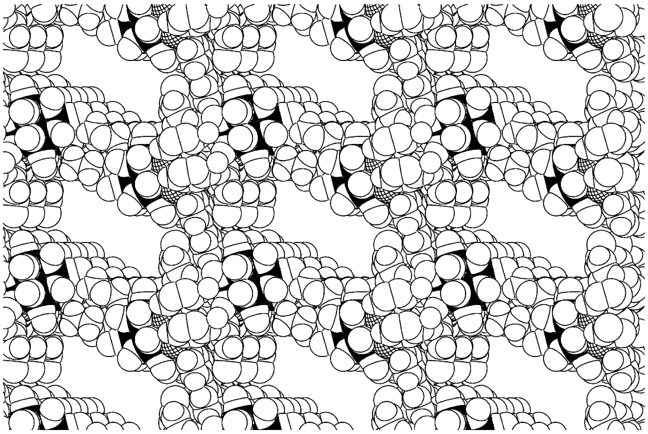

Figure 6. Crystal packing of **2**, viewed along the *c* axis.

that the channels are not filled by other solvent molecules.[19] The calculated density of **2** is also significantly lower than that of **1** (2.34 versus 2.63 g cm^{-3}, respectively).

Conclusions

The presence of nanochannels in **2** suggests several potential applications, mainly connected with the substitution reactivity[20,21] and catalytic properties of carbonylruthenium species.[22] In particular, metal clusters supported on mesoporous materials form nanoparticles, valuable as active and selective catalysts.[23]

Moreover, $[Cu_2TeFe_3(CO)_9(bipy)_{1.5}]$ was found to be a semiconductor. Calculations showed that this property is mainly related to the arrangement of the 4,4′-bipyridyl ligands, which allow electronic communication between the single clusters, increasing the density of states near the HOMO and decreasing the HOMO–LUMO gap of the oligomers.[3] Changes in conductivity of **2** can be hopefully induced by diffusion of doping agents.

Experimental Section

General: All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under oxygen-free nitrogen by using Schlenk-tube techniques.[24] $(NMe_3CH_2Ph)_2[Rh_6C(CO)_{15}]$[25] and $(NEt_4)_2[Ru_6C(CO)_{16}]$[11] were prepared according to literature methods. The diffraction experiments were carried out with a Bruker APEX II CCD area-detector diffractometer. The collected frames were processed with the software SAINT,[26] and an empirical absorption correction was applied (SADABS)[27] to the collected reflections. The calculations were performed by using the Personal Structure Determination Package[28] and the physical constants tabulated therein.[29] The structures were solved by direct methods (SHELXS)[30] and refined by full-matrix least squares using all independent reflections and minimizing the function $\Sigma w(F_o^2 - kF_c^2)^2$ (refinement on F^2). All the non-hydrogen atoms were refined with anisotropic thermal parameters. CCDC-728554 (for **1**) and -728555 (for **2**) 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.

Compound 1: $(NMe_3CH_2Ph)_2[Rh_6C(CO)_{15}]$ (0.095 g, 0.070 mmol) and $AgBF_4$ (0.030 g, 0.154 mmol) (molar ratio 1:2) were dissolved in THF (7 mL), containing a few drops of MeCN. The solution was treated with hexane, filtered, and dried in vacuo. The resulting solid was dissolved in the minimum amount of THF. It was then layered with a solution of pyrazine (0.009 g, 0.113 mmol) in toluene (8 mL). The resulting dark solid, insoluble in most organic solvents, was repeatedly washed with 2-propanol and THF. Yield 0.026 g (25%). IR [ν(CO), ATR]: $\tilde{\nu}$ = 2024 (s), 1871 (m), 1814 (m) cm^{-1}. $C_{28}H_{20}Ag_2N_2O_{17}Rh_6$ (1489.6): calcd. C 22.58, H 1.35, N 1.88; found C 22.52, H 1.45, N 1.91.

Compound 2: This was prepared analogously, from $(NEt_4)_2[Ru_6C(CO)_{16}]$ (0.082 mg, 0.062 mmol), $AgBF_4$ (0.028 g, 0.143 mmol) and 4,4′-bipyridine (0.015 g, 0.096 mmol). Yield 0.057 g (55%). IR [ν(CO), ATR]: $\tilde{\nu}$ = 2062 (w), 2017 (vs), 1994 (s), 1975 (m), 1876 (m) cm^{-1}. $C_{43}H_{28}Ag_2N_3O_{17}Ru_6$ (1680.9): calcd. C 30.73, H 1.68, N 2.50; found C 27.93, H 1.56, N 2.80 (the elemental analysis is in agreement with a partial loss of clathrated toluene: $C_{36}H_{20}Ag_2N_3O_{17}Ru_6$ requires C 27.22, H 1.27, N 2.64).

Supporting Information (see footnote on the first page of this article): Monomeric unit of **2**, including its relation to the THF molecule (Figure S1).

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[16] Crystal data for **1**: M = 1489.64, triclinic, space group $P\bar{1}$, a = 10.7208(8), b = 10.8161(8), c = 16.8329(13) Å, α = 102.163(1), β = 92.567(1), γ = 98.853(1)°, V = 1879.3(3) $Å^3$, T = 150 K, Z = 2, μ = 3.612 mm^{-1}, graphite-monochromatized Mo-K_α radiation (λ = 0.71073 A). Final R indices for 496 parameters: R_2 [F^2, all independent reflections (9479)] = 0.102, wR_2 = 0.119, conventional R_1 = 0.057 for 4806 reflections having $I > 2\sigma(I)$.

[17] Crystal data for **2**: M = 1680.87, monoclinic, space group $P2_1/n$, a = 11.5030(7), b = 17.0428(12), c = 24.7735(15) Å, β = 100.239(1)°, V = 4779.3(6) $Å^3$, T = 150 K, Z = 4, μ = 2.677 mm^{-1}, graphite-monochromatized Mo-K_α radiation (λ = 0.71073 A). Final R indices for 640 parameters: R_2 [F^2, all independent reflections (12695)] = 0.044, wR_2 = 0.073, conventional R_1 = 0.029 for 9457 reflections having $I > 2\sigma(I)$.

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