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Synthesis and characterisation of the chloride-bridged copper–ruthenium cluster dianion $[\{Ru_6Cu_2C(CO)_{16}\}_2Cl_2]^{2-}$

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The mixed-metal ruthenium–copper cluster dianion $[\{Ru_6Cu_2C(CO)_{16}\}_2Cl_2]^{2-}$ **1** has been synthesised in quantitative yield from $[Ru_6C(CO)_{16}]^{2-}$ and CuCl; the crystal structure of the $[N(PPh_3)_2]^+$ salt shows that the two Ru_6 octahedra are linked by a rectangular planar arrangement of copper atoms two opposite edges of which are bridged by chlorine atoms.

Heteronuclear clusters which contain one or more Group 11 metal atoms remain an active area of research.[1] The presence of the Group 11 metals introduces a polarity into the cluster framework that produces metal geometries not observed in homometal clusters.[2] Mixed-metal clusters which contain copper are usually prepared by the reaction of a cationic copper complex with an anionic cluster anion,[3] and the copper electrophile clips on to the cluster surface with the copper atom occupying either an edge-bridging[4] or a face-capping site.[5] Of particular interest are the products from the reaction of $[Cu(MeCN)_4]^+$ with the hexaruthenium carbido cluster anion $[Ru_6C(CO)_{16}]^{2-}$ and the non-carbido cluster anion $[Ru_6(CO)_{18}]^{2-}$. In the first case, an X-ray analysis of the product, $[Ru_6Cu_2C(CO)_{16}(MeCN)_2]$, shows that one Cu atom caps a triangular face of the Ru_6C core while the second lies adjacent to the first, capping an Ru_2Cu face, with a Cu–Cu distance of 2.693(1) Å.[6] In contrast, in the second case, the crystal structure of the product, $[Ru_6Cu_2(CO)_{18}(PhCN)_2]$, shows that the two Cu atoms cap opposite faces of the Ru_6 octahedron, and there is no direct Cu–Cu interaction.[7] A similar core geometry to this second example is observed in the related non-carbido osmium–copper cluster $[Os_6Cu_2(CO)_{18}I_2]$.[8]

In all the examples of mixed ruthenium–copper clusters given the Cu atom, with a ligand attached, has co-ordinated to the periphery of the ruthenium cluster. There have been some recent cases of high-nuclearity clusters where the Cu atoms have become part of the central cluster core, and have linked ruthenium cluster units together. The first of this type was observed in the boride cluster $[Cu_4\{Ru_4H(CO)_{12}BH\}_2Cl]$, in which two Ru_4B core units are linked by a Cu_4 tetrahedron.[9] We have recently developed a synthetic route to produce cluster anions with the formulations $[Ru_8Cu_7H_2Cl_3(CO)_{24}]^{2-}$ and $[Ru_{12}Cu_6H_2Cl_2(CO)_{34}]^{2-}$,[10] in which Ru_4 units are linked by a Cu_7 unit and Ru_6 units are linked by a Cu_6 unit, respectively. In all these reactions the presence of a chloride is apparently required to stabilise the cluster, and is scavenged from the solvent if not present in the reaction mixture.[10] We now report an extension of this work which involves the direct reaction of $[Ru_6C(CO)_{16}]^{2-}$ with copper(I) chloride to produce the novel mixed-metal cluster anion $[\{Ru_6Cu_2C(CO)_{16}\}_2Cl_2]^{2-}$ **1**, in which two Ru_6C units are linked by a rectangular planar Cu_4 array.

The cluster anion $[\{Ru_6Cu_2C(CO)_{16}\}_2Cl_2]^{2-}$ **1** was synthesised by the reaction of $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ with a 5 molar excess of CuCl, in tetrahydrofuran, under reflux. The reaction was stopped after 4 h and the solution filtered hot through Celite; the solvent was then removed *in vacuo*. The residual brown powder was dissolved in the minimum volume of CH_2Cl_2 and purified by TLC using CH_2Cl_2 as eluent to give **1** as the only product. Spectroscopic and analytical data[†] confirmed the formation of a high-nuclearity mixed-metal anion, and crystals suitable for a single-crystal X-ray analysis were grown from the layered diffusion of ethanol into a CH_2Cl_2 solution of **1**.

The crystal structure[‡] of $[N(PPh_3)_2]_2[\{Ru_6Cu_2C(CO)_{16}\}_2Cl_2]$ consists of discrete cationic and dianionic units separated by normal van der Waals distances. The dianion **1**, which has a crystallographic centre of symmetry at the centre of the Cu_4 rectangular plane, is shown in Fig. 1 with selected bond parameters. The cluster core geometry (Fig. 2) may be described as two octahedral Ru_6C units sandwiching a planar Cu_4Cl_2 unit. One face [Ru(1)Ru(3)Ru(5)] of each Ru_6 unit is asymmetrically capped by the Cu(1) atom and the Cu(2) atom then caps the Ru(1)Ru(3)Cu(1) face in a manner similar to that observed in $[Ru_6Cu_2C(CO)_{16}(MeCN)_2]$.[6] The Cu(1)–Cu(2) distance in **1** is also similar to that [2.693(1) Å] in $[Ru_6Cu_2C(CO)_{16}(MeCN)_2]$. The presence of planar rectangular Cu_4 units is not uncommon in the chemistry of Cu^I, and these rectangles are often supported by halide bridges.[13] In the case of **1** the two chloride-bridged Cu $\cdots$ Cu edges of the rectangle are *ca.* 0.33 Å longer than the unbridged edges although the acute angle at the bridging chlorine is consistent with some Cu $\cdots$ Cu interaction. The chloride-bridged distance in **1** is also much longer than the chloride-bridged Cu–Cu edge of 2.660(2) Å found in $[Cu_4\{Ru_4H(CO)_{12}BH\}_2Cl]$,[9] and the halides appear to be holding the two Ru_6Cu_2 cores together. The Ru–Ru distances within the Ru_6 octahedra in **1** range from 2.808(3) to 3.157(2) Å. The longest edge, Ru(1)–Ru(3), is bridged

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[†] $[N(PPh_3)_2]_2[\{Ru_6Cu_2C(CO)_{16}\}_2Cl_2]$: IR ($CH_2Cl_2$) ν(CO) 2055m (br) and 2021vs cm^{-1} (Found: C, 34.7; H, 1.60; N, 0.70. Calc. for $C_{106}H_{60}Cl_2Cu_4N_2O_{32}P_4Ru_{12}$: C, 36.0; H, 1.70; N, 0.80%).

[‡] Crystal data: $C_{106}H_{60}Cl_2Cu_4N_2O_{32}P_4Ru_{12}$, $M = 3535.34$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.872(6)$, $b = 13.470(6)$, $c = 18.664(9)$ Å, $\alpha = 105.04(4)$, $\beta = 109.57(4)$, $\gamma = 92.73(4)°$, $U = 2912(2)$ Å^3, $T = 293(2)$ K, $Z = 1$, $D_c = 2.016$ Mg m^{-3}, μ(Mo-Kα) = 2.394 mm^{-1}, $F(000) = 1704$. Red plates, crystal dimensions 0.06 × 0.22 × 0.46 mm. 7360 Reflections (2θ < 45°) were collected on a Siemens R3mV diffractometer using Mo-Kα radiation (λ = 0.710 73 Å), graphite monochromator and ω–2θ scans. 6733 Independent reflections ($R_{int} = 0.017$) after a semiempirical absorption correction was applied. The structure was solved using direct methods and subsequent Fourier-difference techniques (SHELXTL PLUS),[11] and refined by full-matrix least squares based on F^2(SHELXL93),[12] with all non-hydrogen atoms assigned anisotropic displacement parameters; phenyl H atoms were fixed in idealised positions and allowed to ride on the relevant C atoms. The refinement converged to $R_1 = 0.061$ for 3893 data with $F > 4\sigma(F)$ and $wR_2 = 0.170$ for all data, goodness of fit = 1.090, and weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 18.32P]$, where $P = (F_o^2 + 2F_c^2)/3$. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/264.

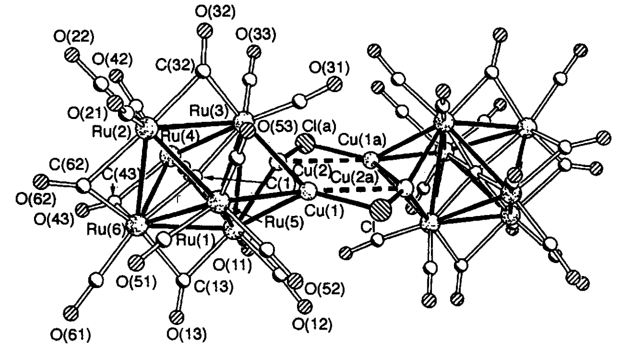

Fig. 1 Molecular structure of the dianion $[\{Ru_6Cu_2C(CO)_{16}\}_2Cl_2]^{2-}$ showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Ru(1)–Cu(2) 2.620(3), Ru(1)–Cu(1) 2.650(3), Ru(1)–Ru(6) 2.837(3), Ru(1)–Ru(5) 2.884(2), Ru(1)–Ru(4) 2.900(2), Ru(1)–Ru(3) 3.157(2), Ru(2)–Ru(3) 2.808(3), Ru(2)–Ru(6) 2.826(3), Ru(2)–Ru(5) 2.874(2), Ru(2)–Ru(4) 2.948(3), Ru(3)–Cu(2) 2.599(3), Ru(3)–Cu(1) 2.611(3), Ru(3)–Ru(5) 2.903(2), Ru(3)–Ru(4) 2.953(3), Ru(4)–Ru(6) 2.829(2), Ru(5)–Cu(1) 2.902(3), Ru(5)–Ru(6) 2.937(3), Cu(1)–Cl 2.198(5), Cu(1)–Cu(2) 2.677(3), Cu(1)–Cu(2a) 3.011(4) and Cu(2)–Cl(a) 2.182(5); Cu(2)–Cu(1)–Cu(2a) 87.45(11), Cu(1)–Cu(2)–Cu(1a) 92.55(11) and Cu(1)–Cl–Cu(2a) 86.9(2)

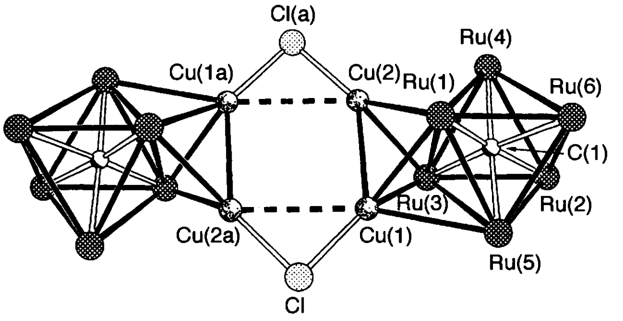

Fig. 2 Core geometry of the $[\{Ru_6Cu_2C(CO)_{16}\}_2Cl_2]^{2-}$ dianion showing the bridging chloride ligands

by both Cu atoms. A similar trend is observed in $[Ru_6Cu_2C(CO)_{16}(MeCN)_2]$[6] where the equivalent distance is 3.072(1) Å. These distances compare to an average Ru–Ru distance of 2.89 Å in the parent dianion $[Ru_6C(CO)_{16}]^{2-}$.[14]

In terms of the charge distribution within **1**, the two '$\{Ru_6C(CO)_{16}\}^{2-}$' units would provide four negative charges and the two chlorides two further negative charges, and as the complex is a dianion overall then each copper atom can be assigned a formal +1 charge, consistent with the observed geometries of the Cu atoms. A similar charge assignment can be made for all the Cu atoms in $[Ru_8Cu_7H_2Cl_3(CO)_{24}]^{2-}$ and $[Ru_{12}Cu_6H_2Cl_2(CO)_{34}]^{2-}$[10] but not in $[Cu_4\{Ru_4H(CO)_{12}BH\}_2Cl]$.[9] It is interesting that in the formation of **1** where CuCl was used the Cu : Cl ratio is 2 : 1 whereas in the formation of $[Ru_8Cu_7H_2Cl_3(CO)_{24}]^{2-}$ and $[Ru_{12}Cu_6H_2Cl_2(CO)_{34}]^{2-}$[10] where the $[Cu(MeCN)_4]^+$ cation is used the Cu : Cl ratios are 7 : 3 and 3 : 1, respectively. Also, when CuCl is used lower-nuclearity Cu-linking clusters are formed.

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