

Supporting Information for

Structural modification in bimetallic Ru(III)-Co(II) metal-organic frameworks

Shenshen Li,^a Yu-Sheng Chen,^b and Karen L. Mulfort*^a

^a*Division of Chemical Sciences and Engineering, Argonne National Laboratory, 9700 South Cass Avenue, Argonne IL 60439;* ^b*ChemMatCARS, Advanced Photon Source, Argonne IL 60439.*

General materials and methods

All reagents and solvents were purchased from Sigma-Aldrich Chemical Company and used without further purification unless otherwise specified. $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{MeOH})_3](\text{OAc})$ was synthesized according to previously reported methods and matched all reported characterization.¹ Ground state absorption spectra were taken in methanol on a Shimadzu UV-1601 spectrophotometer.

Synthetic procedures

$\text{Ru}_3\text{O}(\text{OAc})_6(\text{pyCOOH})_3(\text{PF}_6)$. $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{MeOH})_3](\text{OAc})$ (331 mg, 0.4mmol), 10 equivalents of isonicotinic acid (490 mg, 4mmol), and 10 equivalents of NH_4PF_6 (650 mg, 4mmol) were stirred together in methanol (20ml) at 40°C in a water bath for 18 hours. The product was taken to dryness by rotary evaporation and the residual solid was suspended in 10 mL of methanol and sonicated for 1 minute. The undissolved light-colored solid was removed by vacuum filtration. The filtrate was dried and this procedure was repeated twice with decreasing volumes of methanol to remove extra starting materials. The final product was obtained by recrystallizing the material in methanol/dimethylformamide.

$[\text{Ru}_3\text{O}(\text{OAc})_6(\text{pyCOO})_3]_2[\text{Co}_3(\text{OH})_2]$ (RuCo-1). A methanol solution (100 μL) of $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{pyCOOH})_3](\text{PF}_6)$ (2.6 mg, 0.0025 mmol) and a dimethylacetamide (1 mL) solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.9 mg, 0.01 mmol) were added to a 8 mL vial and heated to 50°C in a stainless steel heating block on top of a programmable hotplate. The temperature was maintained for 200 hours before it was slowly cooled down to 30°C at a rate of 3°C/hour. Dark green single crystals were collected from the crude solid reaction mixture and analyzed by single-crystal X-ray crystallography. The crystals of **RuCo-1** were selected from a reaction mixture which contained a significant amount of insoluble, amorphous material and could not be isolated in a pure quantity for elemental analysis or PXRD. However, we did repeatedly obtain single crystals from follow-up synthesis attempts and collected data on these crystals, which resulted in the identical structure solution as presented in the manuscript.

$[\text{Ru}_3\text{O}(\text{OAc})_6(\text{pyCOO})_3]_6[\text{Ru}_3\text{O}(\text{H}_2\text{O})_3]_2\text{Co}_3(\text{OH})_2\text{X}_6$ (RuCo-2). A methanol solution (100 μL) of $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{pyCOOH})_3](\text{PF}_6)$ (2.6 mg, 0.0025 mmol) and a dimethylacetamide (1 mL) solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.9 mg, 0.01 mmol) were added to an 8 ml vial and left open in a fume hood for 18 hours. The vial was then capped and heated to 80°C in a stainless steel heating block on top of a programmable hotplate. The temperature was maintained for 200 h before it was slowly cooled down to 30°C at a rate of 3°C/hour. Dark green single crystals were collected from the reaction mixture and analyzed by single-crystal X-ray crystallography. The crystals of **RuCo-2** were selected from a reaction mixture which contained a significant amount of insoluble, amorphous material and could not be isolated in a pure quantity for elemental analysis or PXRD. Follow up synthesis efforts yielded very small single crystals with the same morphology, although the crystal quality was not sufficient for structural refinement.

Single crystal data collection and refinement

Single crystal X-ray data of **RuCo-1** and **RuCo-2** were collected at ChemMatCARS, beamline 15ID-B, at temperature of 296(2) K for **RuCo-1** and 100(2) K for **RuCo-2** at the Advanced Photon Source at Argonne National Laboratory. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using *SHELXTL*.² Non-hydrogen atoms were refined with anisotropic displacement

parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{\text{eq}}$ of the attached atom. The solvent molecules of **RuCo-1** and **RuCo-2** are highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions to scattering due to these solvent molecules were removed using the *SQUEEZE* routine of *PLATON* and structures were then refined again using the data generated.³

Table S1. Crystallographic data for **RuCo-1** and **RuCo-2**.

	RuCo-1	RuCo-2
chemical formula	C30 H30 Co1.5 N3 O21 Ru3	C180 H196 Co3 N18 O124 Ru24
formula weight	1160.17	7198.01
crystal system	monoclinic	monoclinic
space group	C2/m	C2/m
a (Å)	21.622(2)	55.289(13)
b (Å)	17.5525(16)	28.916(5)
c (Å)	16.4817(16)	17.468(3)
α (°)	90	90
β (°)	110.836(2)	95.920(5)
γ (°)	90	90
V (Å ³)	5846.0(10)	27778(9)
D_{calc} (g cm ⁻³)	1.318	0.861
Z	4	2
μ (mm ⁻¹)	1.891	1.128
no. of parameters	303	551
reflns collected	11080	11069
reflns ($I > 2\sigma$)	5413	6545
GOF	0.927	1.343
final R ($I > 2\sigma$)	0.0847	0.1287
wR (all data)	0.1482	0.1627

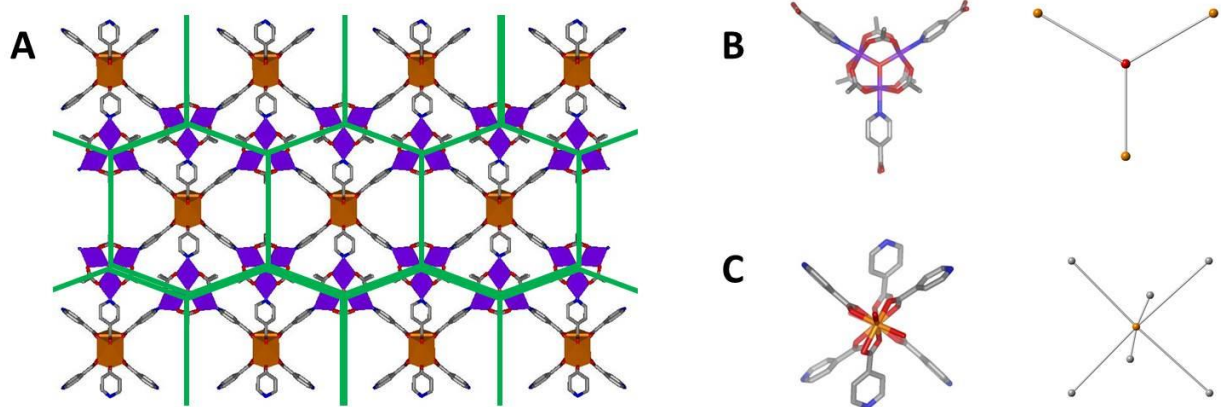
Table S2. Additional bond lengths (Å) and angles (°) for **RuCo-1** and **RuCo-2**.

		RuCo-1	RuCo-2
Co (central)	Co-O ^{eq1}	2.068	2.071
	Co-O ^a	2.100	2.089
	O ^{eq} -Co-O ^{eq1}	88.81 – 92.19	88.96 – 91.04
	O ^a -Co-O ^a	180	180
Co (edge)	Co-O ^h	2.046	2.021
	Co-O ^a	2.098	2.224
	Co-O ^{a'}	2.068 - 2.225	2.137
	Co-O ^{b'}	1.878	1.895
	O ^a -Co-O ^{a'}	54.68 - 57.91	60.61
	O ^{a'} -Co-O ^b /O ^{b'}	90.40 / 116.09 / 136.90 ²	116.86
	O ^{b'} -Co-O ^b	120.7	113.15
	O ^a -Co-O ^h	166.69	169.16
	O ^a -Co- O ^b /O ^{b'}	91.90	89.67
	O ^h -Co- O ^b /O ^{b'}	94.73	98.92
	O ^h -Co-O ^{a'}	113.65 / 108.78 ²	108.55
Ru ₃ O	Ru-μ ₃ -O-Ru	119.68	
		120.13	
		120.13	
Ru ₃ O ^A	Ru-μ ₃ -O-Ru		112.68
			121.94
			125.38
			119.42
Ru ₃ O ^B	Ru-μ ₃ -O-Ru		119.42
			119.42
			121.14

¹ O^{eq} denotes collectively O^a, O^b and O^{b'}.

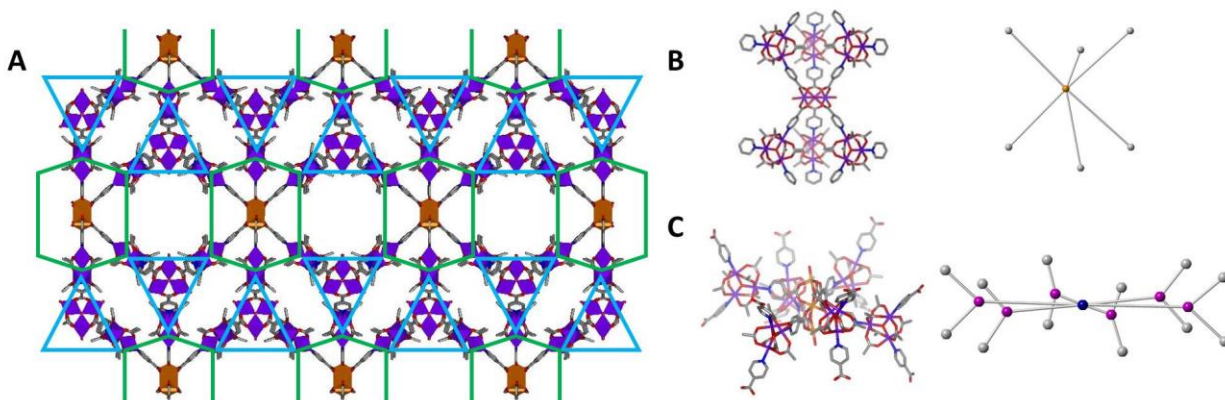
² Different values due to the presence of disorder

Figure S1. Analysis of net connectivity of **RuCo-1**.



A) View of two-dimensional sheets of **RuCo-1**. Green lines indicate hexagonal connectivity. B) Fragment of **RuCo-1** crystal structure, Ru₃O strut, indicating 3-c connectivity. C) Fragment of **RuCo-1** crystal structure, Co₃ node, indicating 6-c connectivity.

Figure S2. Analysis of net connectivity of **RuCo-2**.



A) View of two-dimensional sheets of **RuCo-2** down *c* axis. Green and blue lines indicate connectivity. B) Fragment of **RuCo-2** crystal structure, Ru₃O^B strut, indicating 6-c connectivity. C) Fragment of **RuCo-2** crystal structure, [Co₃][Ru₃O^A]₆ node, indicating 12-c connectivity.

References

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