Electronic Supporting Information (ESI)

Homo-valent diruthenium(II,II) carbonates $Na_4[Ru_2(CO_3)_4]\cdot 10H_2O$: synthesis, structure, properties, and calculation

Jing-Yu Li, Pei Zhang, Jian-Hui Yang and Bin Liu*

Key Laboratory of Synthetic and Natural Functional Molecule of the Ministry of Education, Xi'an Key Laboratory of Functional Supramolecular Structure and Materials, College of Chemistry & Materials Science, Northwest University, Xi'an 710127, P. R. China

Table S1. Crystal data and structural refinement parameters for compound **1**

Compound **1**	
Empirical formula	$C_4H_{20}Na_4O_{22}Ru_2$
Formula weight	714.30
Temperature (K)	150(2)
Wavelength (Å)	1.34139
Crystal system	Monoclinic
Space group	*C*2/*c*
a /Å	23.0029(12)
b /Å	9.0127(4)
c /Å	9.9585(5)
β/°	107.461(2)
V/Å^3	1869.45(17)
Z	4
ρ_{calc} (g ·cm^{-3})	2.409
μ (mm^{-1})	12.561
F (000)	1408
Reflections collected	10766
Reflections unique	1739
parameters	146
GOF on F^2	1.042
R_{int}	0.055
R_1, $wR_2{}^a$ [$I>2\sigma(I)$]	0.0530, 0.1422
R_1, $wR_2{}^a$ (all data)	0.0555, 0.1442
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e/Å^3]	2.486, -1.404

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

* Corresponding author. Tel./fax: +86-029-81535026.

E-mail address: liubin@nwu.edu.cn (B. Liu).

Table S2. Selected bond distances (Å) for compound **1**

Selected bond distances (Å)					
Ru(1)–Ru(1k)	2.2572(7)	Na(1)–O(6)	2.351(5)	Na(2)–O(8)	2.412(7)
Ru(1)–O(1k)	2.077(5)	Na(1)–O(7)	2.372(6)	Na(2)–O(9)	2.373(11)
Ru(1)–O(2)	2.082(5)	Na(1)–O(8)	2.360(6)	Na(2)–O(10)	2.529(13)
Ru(1)–O(4)	2.073(5)	Na(1)–O(2a)	2.446(5)	Na(2)–O(11)	2.332(11)
Ru(1)–O(5k)	2.086(5)	Na(1)–O(4h)	2.331(6)	Na(2)–O(3f)	2.586(8)
Ru(1)–O(6i)	2.323(5)	Na(1)–O(5j)	2.470(6)	Na(2)–O(9c)	2.487(14)
C(1)–O(1)	1.306(9)	C(1)–O(2)	1.290(9)	C(1)–O(3)	1.272(10)
C(2)–O(4)	1.285(9)	C(2)–O(5)	1.306(8)	C(2)–O(6)	1.261(8)

Table S3. Selected angles (˚) for compound **1**

Ru(1k)–Ru(1)–O(2)	89.85(13)	Ru(1k)–O(1)–C(1)	119.6(4)
Ru(1k)–Ru(1)–O(4)	89.21(14)	Ru(1k)–O(5)–C(2)	118.7(4)
Ru(1k)–Ru(1)–O(1k)	89.97(14)	Ru(1h)–O(6)–C(2)	126.1(4)
Ru(1k)–Ru(1)–O(5k)	90.41(13)	Ru(1)–O(2)–C(1)	119.9(4)
Ru(1k)–Ru(1)–O(6i)	172.61(12)	Ru(1)–O(4)–C(2)	121.2(4)
O(2)–Ru(1)–O(4)	87.62(19)	O(1k)–Ru(1)–O(4)	92.5(2)
O(2)–Ru(1)–O(6i)	89.96(18)	O(4)–Ru(1)–O(5k)	178.48(19)
O(1k)–Ru(1)–O(2)	179.8(2)	O(1k)–Ru(1)–O(6i)	90.23(18)
O(2)–Ru(1)–O(5k)	90.90(18)	O(5k)–Ru(1)–O(6i)	96.99(17)
O(4)–Ru(1)–O(6i)	83.40(18)	O(1k)–Ru(1)–O(5k)	89.0(2)
O(2)–C(1)–O(3)	119.4(7)	O(4)–C(2)–O(6)	121.4(6)
O(1)–C(1)–O(2)	120.2(6)	O(5)–C(2)–O(6)	118.6(6)
O(1)–C(1)–O(3)	120.4(7)	O(4)–C(2)–O(5)	120.0(6)
O(6)–Na(1)–O(7)	87.8(2)	O(8)–Na(2)–O(9)	75.5(4)
O(6)–Na(1)–O(8)	86.4(2)	O(8)–Na(2)–O(10)	102.6(3)
O(2a)–Na(1)–O(6)	155.4(2)	O(8)–Na(2)–O(11)	87.9(3)
O(4h)–Na(1)–O(6)	77.5(2)	O(8)–Na(2)–O(9c)	163.2(3)
O(5j)–Na(1)–O(6)	119.8(2)	O(3f)–Na(2)–O(8)	96.5(3)
O(7)–Na(1)–O(8)	90.3(2)	O(9)–Na(2)–O(10)	79.3(3)
O(2a)–Na(1)–O(7)	79.21(19)	O(9)–Na(2)–O(11)	89.1(4)
O(4h)–Na(1)–O(7)	101.4(2)	O(9)–Na(2)–O(9c)	88.1(4)
O(5j)–Na(1)–O(7)	152.4(2)	O(3f)–Na(2)–O(9)	170.3(4)
O(2a)–Na(1)–O(8)	114.2(2)	O(10)–Na(2)–O(11)	161.8(4)
O(4h)–Na(1)–O(8)	159.6(2)	O(9c)–Na(2)–O(10)	77.2(3)
O(5j)–Na(1)–O(8)	93.2(2)	O(3f)–Na(2)–O(10)	97.4(3)
O(2a)–Na(1)–O(4h)	84.62(19)	O(9c)–Na(2)–O(11)	88.4(4)
O(2a)–Na(1)–O(5j)	74.34(17)	O(3f)–Na(2)–O(11)	96.2(3)

O(4h)–Na(1)–O(5j)	84.17(19)	O(3f)–Na(2)–O(9c)	100.2(3)

Symmetry codes: a x,-1+y,z; b x,1+y,z; c 1-x,y,3/2-z; d -x,1-y,-z; e x,1-y,-1/2+z; f x,1-y,1/2+z; g -1/2+x,1/2+y,z; h 1/2-x,-1/2+y,1/2-z; i 1/2-x,1/2+y,1/2-z; j 1/2-x,1/2-y,1-z; k 1/2-x,3/2-y,1-z.

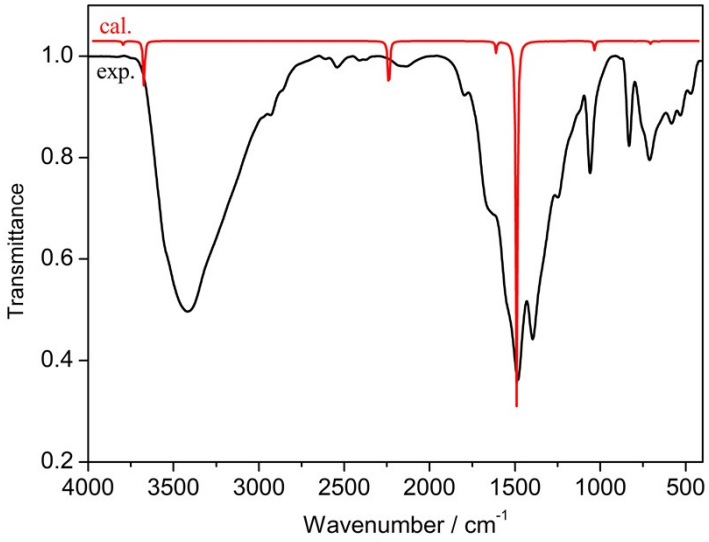

Fig. S1 IR spectrum of compound **1**.

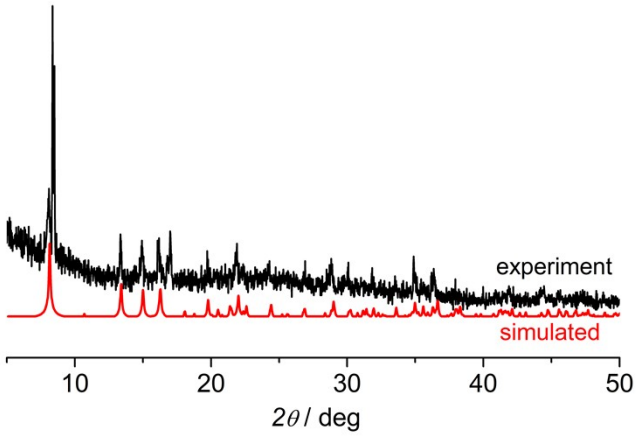

Fig. S2 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized bulk samples of **1.**

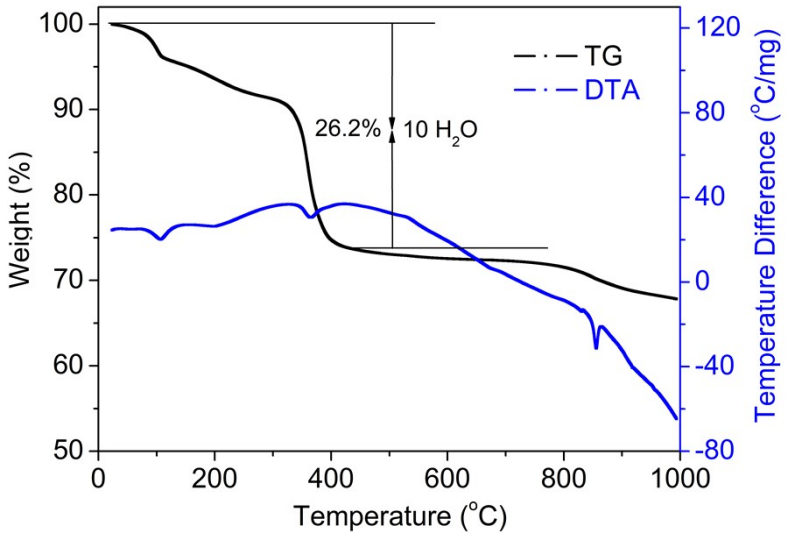

Fig. S3 TG curve of compound **1**.

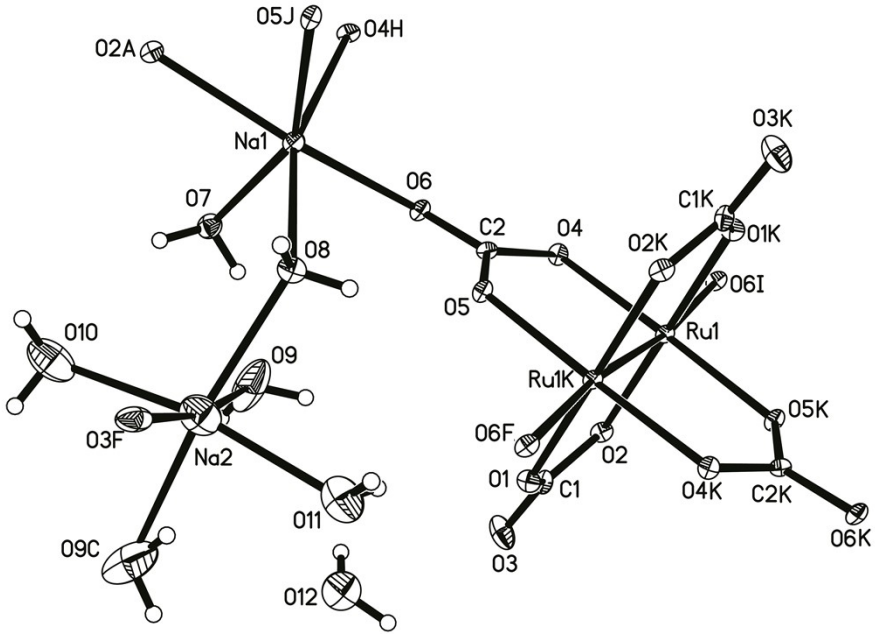

Fig. S4 ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of **1.**

Table S4. Selected bond distances (Å) from the experiment and calculation.

	Exp.	Calc.		Exp.	Calc
Ru(1)–Ru(1K)	2.2572(7)	2.26366	C(1)–O(1)	1.306(9)	1.31183
Ru(1)–O(4)	2.073(5)	2.10847	C(1)–O(2)	1.290(9)	1.31183
Ru(1)–O(2)	2.082(5)	2.10847	C(1)–O(3)	1.272(10)	1.27212
Ru(1)–O(5A)	2.086(5)	2.10680	C(2)–O(4)	1.285(9)	1.31252
Ru(1)–O(1K)	2.077(5)	2.10680	C(2)–O(5)	1.306(8)	1.31252
Ru(1)–O(6I)	2.323(5)	2.55332	C(2)–O(6)	1.261(8)	1.27154

Table S5. Selected frontier orbital data for the model anion $[Ru_2(CO_3)_4(H_2O)_2]^{4-}$ derived from the open-shell electronic structure DFT calculation in vacuum.

	α			β	
	Orbital	Energy(eV)		Orbital	Energy(eV)
90	σ*(LUMO)	-0.41104	91	σ*	-0.31866
89	δ*(HOMO)	-3.73671	89	π*	-0.88642
88	π*	-4.03267	88	π*(LUMO)	-0.95367
87	π*	-4.07975	87	δ*(HOMO)	-3.31065
86	δ	-4.47398	86	δ	-4.10503
80	π	-6.37308	85	π	-4.89803
79	π	-6.41177	84	π	-4.9459
77	σ	-6.47309	80	σ	-6.1597

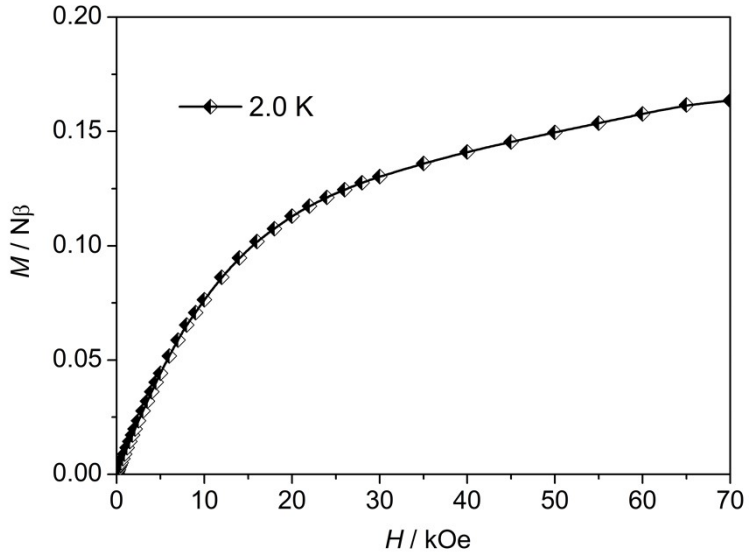

Fig. S5. *M* versus *H* data of compound **1**.

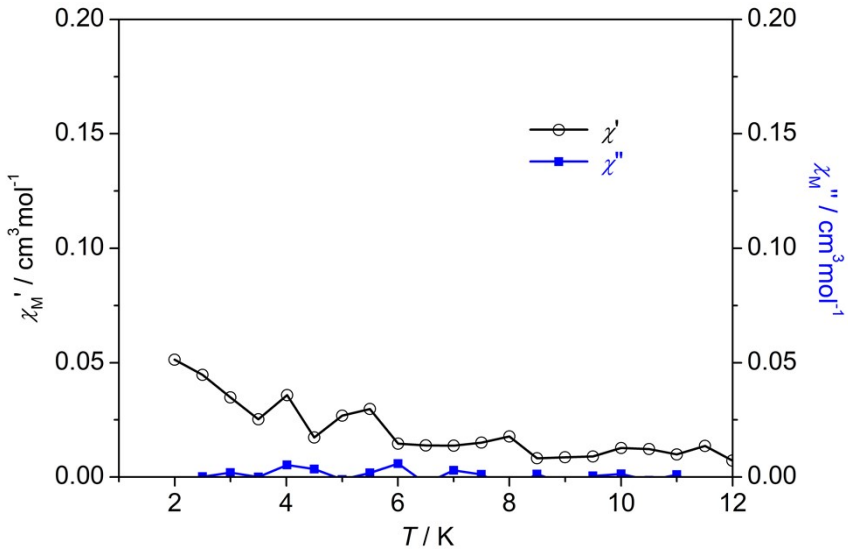

Table S6. The calculated vibration frequency corresponds to the Raman Activity

Freq	Raman Activity	Freq	Raman Activity
68.10	1991.7323	689.60	57.4805
80.06	44.7549	698.94	582.2816
126.39	38224.8266	712.07	18.6536
153.85	443.7272	714.18	5.6683
155.09	369.5587	807.42	6.2210
199.66	125.8802	829.52	3.2284
205.41	853.2098	1053.30	15.0955
245.79	45.3903	1057.90	48.3333
254.94	74.7289	1300.31	2960.5491
281.12	91.2578	1301.20	4606.7600
292.58	798.5226	1509.47	73.4025
301.01	522.1881	1552.69	582.7461
306.85	302.9056	1637.71	2518.6907
378.52	1974.9080		

Table S7. The calculated vibration frequency corresponds to the Infrared Absorption

Freq	Infrared	**Freq**	Infrared
231.98	15.5692	816.11	1.1397
241.40	20.9410	1056.53	42.8631
243.00	6.3062	1057.29	41.1559
243.72	10.6011	1513.08	1742.7237
347.16	84.1287	1514.33	1636.4498
354.47	91.9147	1634.45	98.8444
403.92	5.1138	2264.63	541.1406
682.95	1.8426	3701.58	429.5674
684.26	2.7051	3824.45	33.6617
728.47	24.5336		

Table S8. The representative calculated optical transitions for anion $Ru_2(CO_3)_4(H_2O)_2^{4-}$.

λ(nm)	f	assign.	%
484.99	0.0122	π→π*	40
319.23	0.0022	π*→$P_{C,O}$	96
318.47	0.0011	π*→$P_{C,O}$	96
314.92	0.0014	δ→$P_{C,O}$	92
311.71	0.0014	δ→$P_{C,O}$	84
279.73	0.0127	Pc,o→σ*	82
268.26	0.0057	Pc,o→σ*	93
267.31	0.0045	Pc,o→σ*	93
261.10	0.0015	π*→σ*	92
244.06	0.0111	Pc,o→σ*	82
243.26	0.0110	Pc,o→σ*	81
233.66	0.0081	Pc,o→π*	86
233.01	0.0040	Pc,o→σ*	68
232.04	0.0958	σ→σ*	64