The cyclo-Sb$_6$ Ring in the [Sb$_6$(RuCp*)$_2$]$^{2-}$ Ion

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Experimental Section

General Data. All reactions were carried out in a nitrogen atmosphere dry-box (Vacuum Atmosphere Co.) or using standard Schlenk-line techniques. The matrix-assisted laser desorption/ionization time-of-flight (MALDI–TOF, Bruker Autoflex Speed) mass spectra were recorded in the negative ion mode with 2KHz smart beam II laser. All the NMR experiment was performed on a Bruker AV-400 MHz spectrometer at room temperature. ^{1}H NMR and ^{13}C NMR spectra were calibrated to residual ^{1}H and ^{13}C chemical shifts of pyridine-d_5, respectively.

Chemicals

K (Sigma-Aldrich, 99%), Na (Sigma-Aldrich, 99.7%), Sb (Sigma-Aldrich, 99.999%), chloro(pentamethylcyclopentadienyl)(cyclooctadiene)ruthenium(II) (Cp*RuCl(COD), Sigma-Aldrich) and benzophenone (Aldrich, 99.5%) were used as received. Melts of nominal composition of "K$_3$Sb" were prepared by fusion of stoichiometric ratios of the elements at high temperature (~1100 °C). The elements were loaded into quartz tubes in a nitrogen atmosphere dry box and then sealed under vacuum. CAUTION: the fusion process can be very exothermic and the reactions should be conducted behind blast shields on small scales (<10g) using full protective gear. 4,7,13,16,21,24-Hexaoxa-1,10-diazobicyclo[8,8,8]hexacosane (2,2,2-crypt) were purchased from Fisher Scientific. Anhydrous ethylenediamine (en) was vacuum distilled from K$_4$Sn$_9$, and stored under dinitrogen. Toluene was distilled from sodium/benzophenone under dinitrogen and stored under dinitrogen.

Synthesis of [K([2.2.2]crypt)]$_2$[Sb$_6$(RuCp*)$_2$]•2tol. 49.3mg (0.21 mmol) of "K$_3$Sb" and 160.8 mg (0.43 mmol) of [2.2.2]crypt were weighed out into a 10 mL scintillation vial. Then ca. 3 mL of ethylenediamine was added. The reaction mixture was stirred for 20 min, resulting in a dark brown-green solution, to which 2ml brown/orange toluene solution of Cp*RuCl(cod) (38.0mg, 0.1mmol) was added dropwise. The reaction mixture was then stirred for 1.5h, then heated at 60°C for 1h and at 65°C for another 1.5h. The resulting dark brown-red solution was subsequently centrifuged and filtered through glass wool and transferred to a test tube, and then carefully layered with toluene (3 mL). After about a week, big black-red tabular crystals of [K([2.2.2]crypt)]$_2$[Sb$_6$(RuCp*)$_2$]•2tol were obtained in approximately 30% yield (based on the precursor "K$_3$Sb").

Synthesis of [K([2.2.2]crypt)]$_2$[Sb$_6$(RuCp*)$_2$]•tol•py (2) 15.3 mg of crystalline [K([2.2.2]crypt)]$_2$[Sb$_6$(RuCp*)$_2$]•2tol were dissolved in 0.5ml deuterated pyridine in an NMR tube, resulting in a dark red solution. After layering the solution with toluene, black-red blocks of [K([2.2.2]crypt)]$_2$[Sb$_6$(RuCp*)$_2$]•tol•py were isolated after two weeks (7.3mg, yield 47.7%).

Crystallographic Studies (1) A suitable single crystals of $C_{70}H_{118}K_2N_4O_{12}Ru_2Sb_6$ (UM3011) was selected and measured on a Bruker Smart Apex2 diffractometer.[1] The crystal was kept at 150(2) K during data collection. The integral intensity was correct for absorption using SADABS software [2] using multi-scan method. Resulting minimum and maximum transmission are 0.691 and 0.789 respectively. The structure was solved with the ShelXS-2015 (Sheldrick, 2015c) program and refined with the ShelXL-2015 (Sheldrick, 2015c) program and least-square minimisation using ShelX software package.[3-5] Number of restraints used = 758.

(2) A suitable single crystals of C68H115K2N5O12Ru2Sb6 (UM3072) was selected and measured on a diffractometer.[1] The crystal was kept at 150(2) K during data collection. The integral intensities were corrected for absorption using SADABS software[2] using multi-scan method. Resulting minimum and maximum transmission are 0.659 and 0.806 respectively. The structure was solved with the ShelXS-2015 (Sheldrick, 2015c) program and refined with the ShelXL-2015 (Sheldrick, 2015c) program and least-square minimisation using ShelX software package.[3-5] Number of restraints used = 333.

Crystal structure determination:

(**1**) *Crystal Data* for $C_{70}H_{118}K_2N_4O_{12}Ru_2Sb_6$ (M =2218.52 g/mol): triclinic, space group P-1 (no. 2), a = 13.0477(11) Å, b = 14.1374(12) Å, c = 23.620(2) Å, α = 87.7781(14)°, β = 84.4934(13)°, γ = 79.1444(14)°, V = 4258.2(6) Å^3, Z = 2, T = 150(2) K, μ(MoKα) = 2.369 mm^{-1}, D_{calc}= 1.730 g/cm^3, 101412 reflections measured (3.192° ≤ 2Θ ≤ 62.998°), 27856 unique (R_{int} = 0.0276, R$_{sig}$ = 0.0339) which were used in all calculations. The final R_1 was 0.0248 (I > 2σ(I)) and wR_2 was 0.0572 (all data).

(**2**) *Crystal Data* for $C_{68}H_{110}D_5K_2N_5O_{12}Ru_2Sb_6$ (M =2205.48 g/mol): triclinic, space group P-1 (no. 2), a = 13.1437(9) Å, b = 13.9600(10) Å, c = 23.4840(16) Å, α = 88.5283(11)°, β = 84.7546(11)°, γ = 79.2296(11)°, V = 4215.2(5) Å^3, Z = 2, T = 150(2) K, μ(MoKα) = 2.393 mm^{-1}, D_{calc} = 1.738 g/cm3, 62159 reflections measured (3.166° ≤2Θ≤ 60°), 24389 unique (R_{int} = 0.0207, R_{sig} = 0.0280) which were used in all calculations. The final R_1 was 0.0279 (I > 2σ(I)) and wR_2 was 0.0551 (all data).

References:

1. Bruker (2010). Apex2. Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M. (2008), *Acta Cryst.* **A64**, 112-122.
3. Sheldrick, G. M. (2014). SHELXL-2014. University of Gottingen, Germany.
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DFT Calculations were performed using the Gaussian 09 program package (Revision A.02) [6] and crystal structure parameters. All DFT calculations were carried out using the B3LYP functional, that is, Beck's hybrid three-parameter exchange functional [7] with the Lee-Yang-Parr correlation functional.[8] In these calculations, the solvent effects were taken into account by the Polarizable Contiuum Model.[9]

References:

6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G.

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7. D. Becke, *J. Chem. Phys*. 1993**, 98**, 5648.
8. Lee, W. Yang and R. G. Parr*, Phys. Rev. B.* 1988, **37**, 785.
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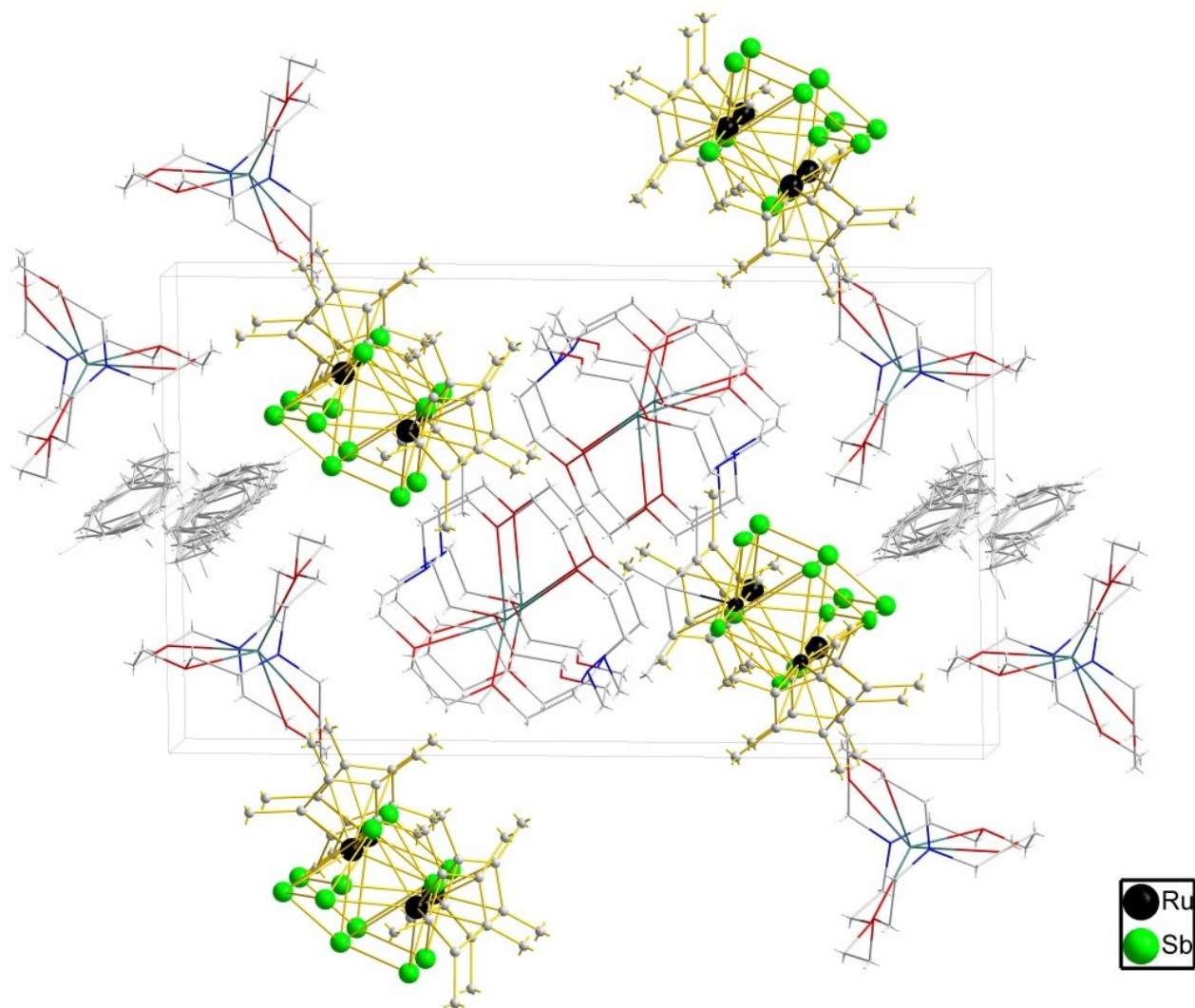
Figure S1. View of **[**K([2.2.2]crypt)]₂[Sb₆(RuCp*)₂]•2tol down the *a* axis. (H atoms were set invisible for clarity).

Table S1 Selected crystallographic data collection, and refinement data for $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2]\cdot 2tol$ (**1**) and $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2]\cdot tol\cdot py$ (**2**).

Empirical formula	$C_{70}H_{118}K_2N_4O_{12}Ru_2Sb_6$	$C_{68}H_{115}K_2N_5O_{12}Ru_2Sb_6$
Formula weight	2218.52	2205.48
Temperature/K	150(2)	150(2)
Crystal system	triclinic	triclinic
Space group	P -1	P -1
a/Å	13.0477(11)	13.1437(9)
b/Å	14.1374(12)	13.9600(10)
c/Å	23.620(2)	23.4840(16)
α/°	87.7781(14)	88.5283(11)
β/°	84.4934(13)	84.7546(11)
γ/°	79.1444(14)	79.2296(11)
Volume/Å^3	4258.2(6)	4215.2(5)
Z	2	2
ρ_{cal} cg/cm^3	1.730	1.738
μ/mm^{-1}	2.369	2.393
$F(000)$	2188.0	2172.0
Crystal size/mm^3	0.26 × 0.105 × 0.10	0.26 × 0.19 × 0.09
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.192 to 62.998	3.166 to 60
Index ranges	$-19 \leqslant h \leqslant 19$, $-20 \leqslant k \leqslant 20$, $-34 \leqslant l \leqslant 34$	$-18 \leqslant h \leqslant 18$, $-19 \leqslant k \leqslant 19$, $-33 \leqslant l \leqslant 33$
Reflections collected	101412	62159
Independent reflections	27856 [R_{int} = 0.0854, R_{sigma} = 0.0709]	24389 [R_{int} = 0.0207, R_{sigma} = 0.0280]
Data/restraints/parameters	27856/758/968	24389/333/906
Goodness-of-fit on F^2	1.001	1.157
R_1/wR_2 [$I>=2\sigma(I)$]	0.0248/0.0552	0.0279/0.0527
R_1/wR_2 [all data]	0.0371/0.0572	0.0409/ 0.0551

Table S2 Selected bond lengths(angstroms) and bond angles(degree) of $[Sb_6Ru_2(Cp^*)_2]^{2-}$ in $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2] \cdot 2tol$ (**1**) and $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2] \cdot tol \cdot py$ (**2**).

Bonds(Å)	1	2
Sb1–Sb2	2.7878(2)	2.7885(3)
Sb1–Sb3	2.8371(3)	2.8378(3)
Sb2–Sb5	2.9538(2)	2.9501(3)
Sb3–Sb4	2.7324(2)	2.7342(3)
Sb4–Sb6	2.8519(3)	2.8596(3)
Sb5–Sb6	2.7886(3)	2.7909(3)
Ru1–Sb6	2.6848(3)	2.6871(3)
Ru1–Sb1	2.6872(3)	2.6907(3)
Ru1–Sb2	2.7634(3)	2.7619(3)
Ru1–Sb5	2.7903(3)	2.7915(3)
Ru2–Sb2	2.6969(3)	2.6945(3)
Ru2–Sb3	2.7093(3)	2.7123(3)
Ru2–Sb4	2.7094(3)	2.7077(3)
Ru2–Sb5	2.7175(3)	2.7173(3)
Angles(°)	**1**	**2**
Sb2–Ru2–Sb5	66.125(6)	66.065(7)
Sb3–Ru2–Sb5	108.951(9)	109.022(10)
Sb4–Ru2–Sb5	76.843(6)	76.683(8)
Ru1–Sb1–Sb2	60.594(6)	60.507(7)
Ru1–Sb1–Sb3	106.736(7)	106.864(9)
Sb2–Sb1–Sb3	73.507(7)	73.534(8)
Ru2–Sb2–Ru1	104.079(8)	104.260(9)
Ru2–Sb2–Sb1	101.521(8)	101.560(9)
Ru1–Sb2–Sb1	57.902(7)	57.994(8)
Ru2–Sb2–Sb5	57.272(6)	57.338(7)
Ru1–Sb2–Sb5	58.311(7)	58.401(7)
Sb1–Sb2–Sb5	101.083(8)	101.182(9)
Ru2–Sb3–Sb4	59.722(7)	59.620(8)
Ru2–Sb3–Sb1	99.961(8)	99.868(10)
Sb4–Sb3–Sb1	102.993(7)	102.689(9)
Ru2–Sb4–Sb3	59.716(6)	59.786(8)
Ru2–Sb4–Sb6	99.727(7)	99.989(8)
Sb3–Sb4–Sb6	102.193(9)	102.637(9)
Ru2–Sb5–Sb6	101.128(7)	101.495(9)
Ru2–Sb5–Ru1	102.820(7)	102.867(9)
Sb6–Sb5–Ru1	57.534(5)	57.547(7)
Ru2–Sb5–Sb2	56.603(6)	56.597(8)
Sb6–Sb5–Sb2	99.972(8)	100.160(9)
Ru1–Sb5–Sb2	57.428(5)	57.425(7)
Ru1–Sb6–Sb5	61.266(8)	61.239(8)
Ru1–Sb6–Sb4	106.818(8)	106.347(9)

Sb5-Sb6-Sb4	73.431(6)	73.099(8)
Sb6-Ru1-Sb1	95.378(7)	95.579(8)
Sb6-Ru1-Sb2	107.690(9)	107.845(10)
Sb1-Ru1-Sb2	61.504(6)	61.499(7)
Sb6-Ru1-Sb5	61.200(7)	61.214(8)
Sb1-Ru1-Sb5	108.088(7)	107.977(8)
Sb2-Ru1-Sb5	64.261(6)	64.173(7)
Sb2-Ru2-Sb3	77.016(8)	77.057(9)
Sb2-Ru2-Sb4	108.863(7)	108.646(9)
Sb3-Ru2-Sb4	60.563(6)	60.593(7)

Table S3 Selected bond lengths(angstroms) of the Sb_6Ru_2 Core in $[Sb_6Ru_2(Cp*)_2]^{2-}$(1) and $[Sb_6Ru_2(Cp)_2]^{2-}$(calculation)

Bonds(Å)	1	Calculation
Sb1-Sb2	2.7878(2)	2.88265
Sb1-Sb3	2.8371(3)	2.95071
Sb2-Sb5	2.9538(2)	3.03700
Sb3-Sb4	2.7324(2)	2.82118
Sb4-Sb6	2.8519(3)	2.95073
Sb5-Sb6	2.7886(3)	2.88251
Ru1-Sb1	2.6872(3)	2.74650
Ru1-Sb2	2.7634(3)	2.85037
Ru1-Sb5	2.7903(3)	2.85018
Ru1-Sb6	2.6848(3)	2.74675
Ru2-Sb2	2.6969(3)	2.76542
Ru2-Sb3	2.7093(3)	2.78880
Ru2-Sb4	2.7094(3)	2.78881
Ru2-Sb5	2.7175(3)	2.76534

Table S4 Mulliken atomic charges of metal atoms.

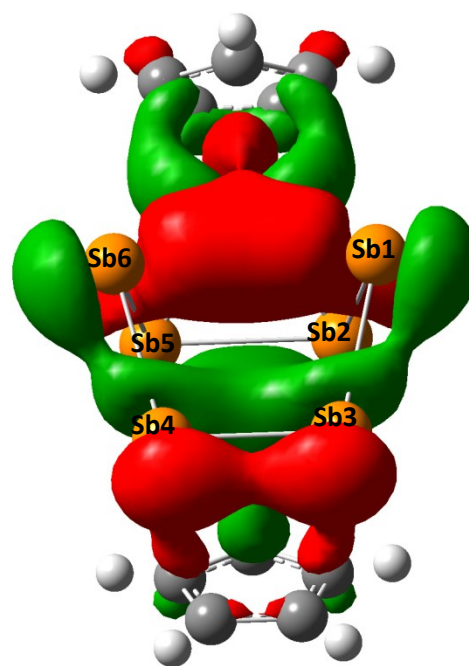| Atom	Charge
Ru1	-0.846552
Ru2	-0.863576
Sb1	-0.180091
Sb2	0.159938
Sb3	-0.137681
Sb4	-0.137702
Sb5	0.160029
Sb6	-0.180249
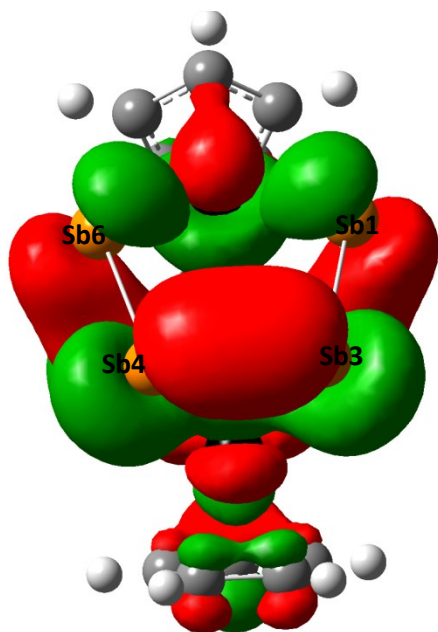
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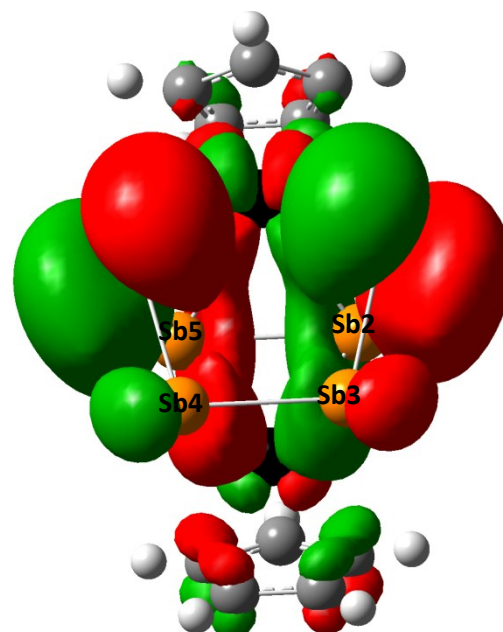
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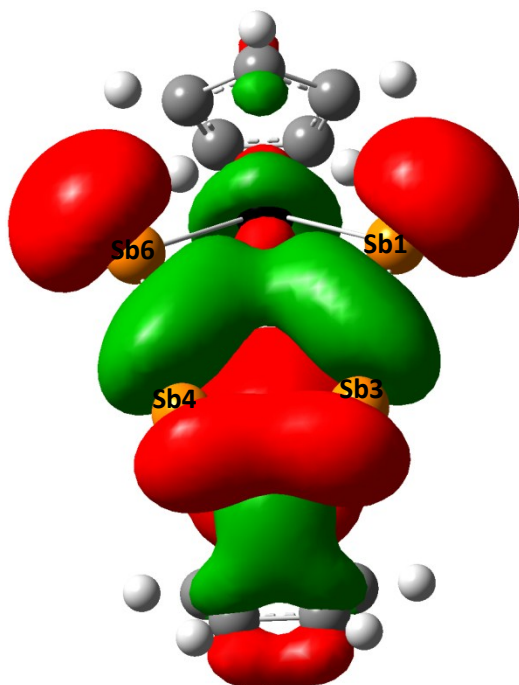
(c) HOMO-4

(d) HOMO-5

Figure S2 Frontier molecular orbital of $[Sb_6Ru_2(Cp)_2]^{2-}$. All drawing use the atomic labelling scheme shown in **Fig. 1.**

Energy dispersive X-ray spectroscopy (EDX) analysis

EDX analysis on [K([2.2.2]crypt)]$_2$[Sb$_6$(RuCp*)$_2$]•2tol was performed on Hitachi SU-70 SEM, operated at an acceleration voltage of 10 keV. Data acquisition was performed with an accumulation time of 120 s. The atomic ratio of K/Ru/Sb is 2.037/5.951/1.975(**Table S5**), which is in good agreement with experimental crystallographic data.

Table S5 EDX analysis of [K([2.2.2]crypt)]$_2$[Sb$_6$(RuCp*)$_2$]•2tol.

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
C	6	K-series	24859	32.63832	35.63419	64.81635	3.70285
Sb	51	L-series	11450	30.32503	33.10856	**5.940776**	1.02798
O	8	K-series	7374	16.92452	18.47801	25.23181	2.111642
Ru	44	L-series	5791	8.366653	9.134626	**1.974537**	0.311051
K	19	K-series	2436	3.338202	3.644614	**2.036529**	0.135176
			Sum:	91.59273	100	100	
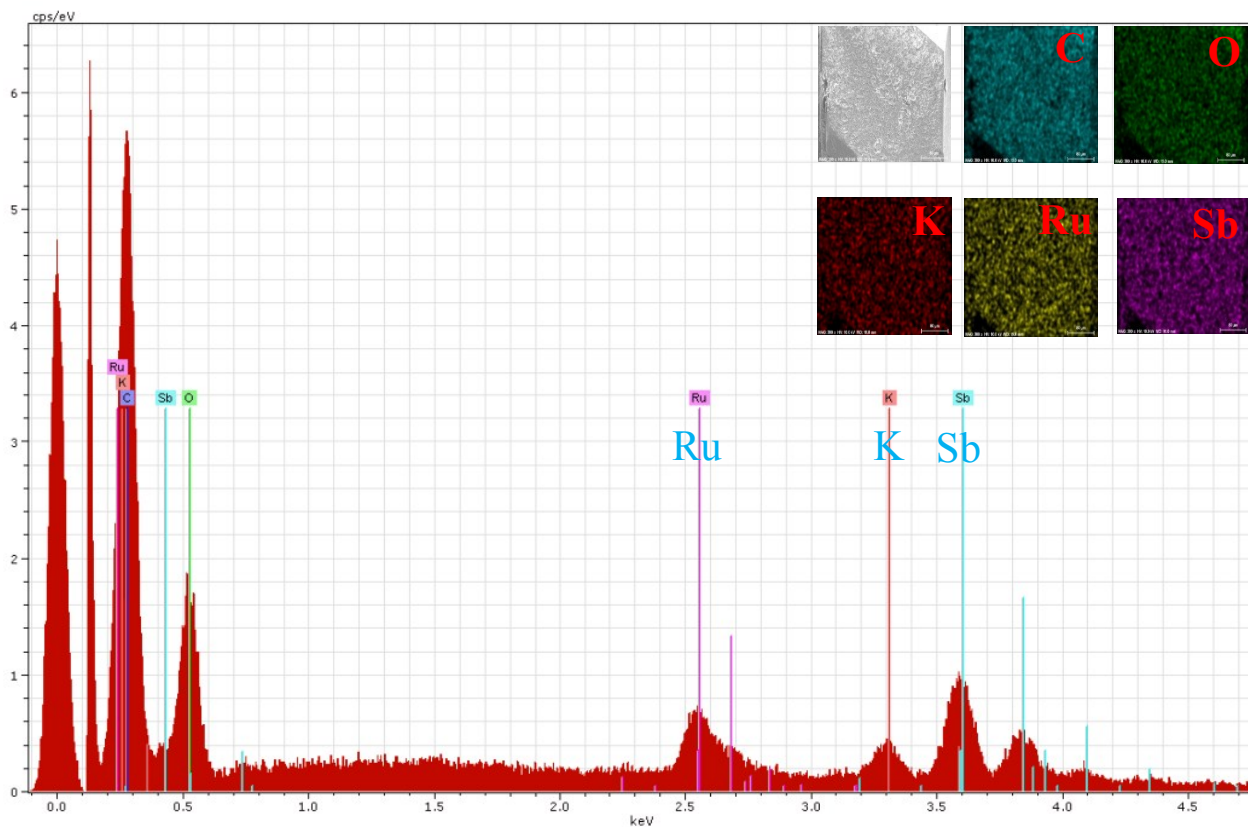
Figure S3 EDX analysis of [K([2.2.2]crypt)]$_2$[Sb$_6$(RuCp*)$_2$]•2tol with the elemental mapping inserted.
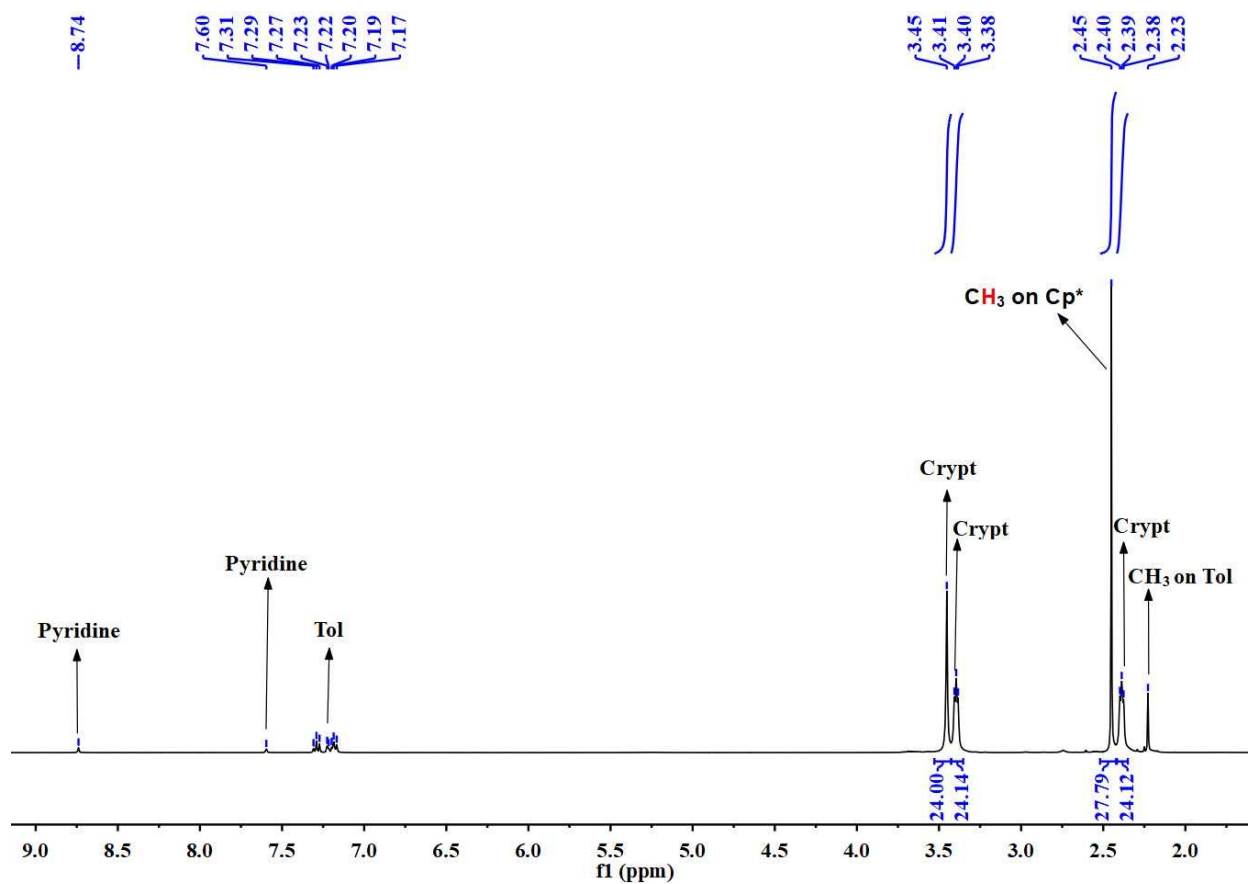
Figure S4 ^{1}H NMR of crystal sample in deuterated pyridine. The data were collected at 400 MHz and room temperature.
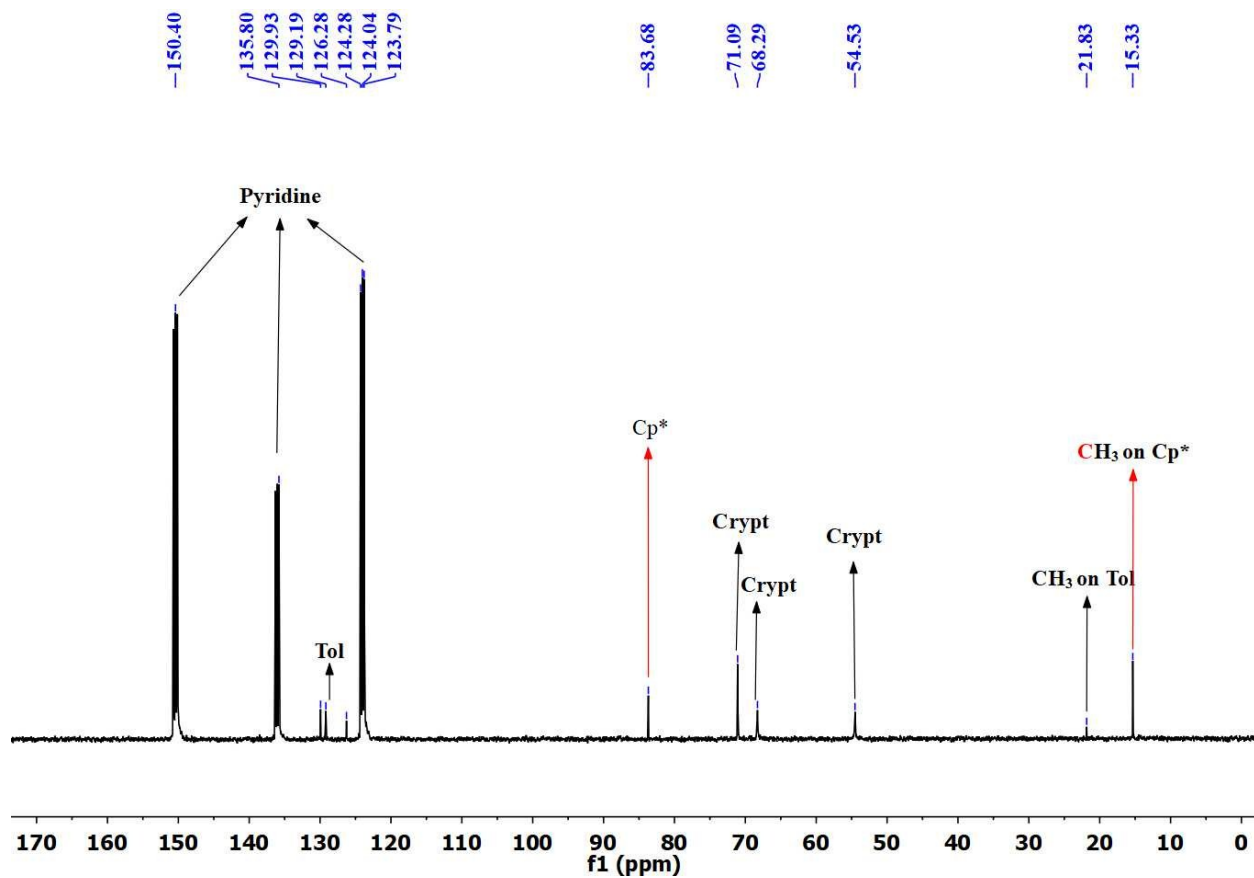
Figure S5 ^{13}C NMR of crystal sample in deuterated pyridine. The data were collected at 101MHz and room temperature.
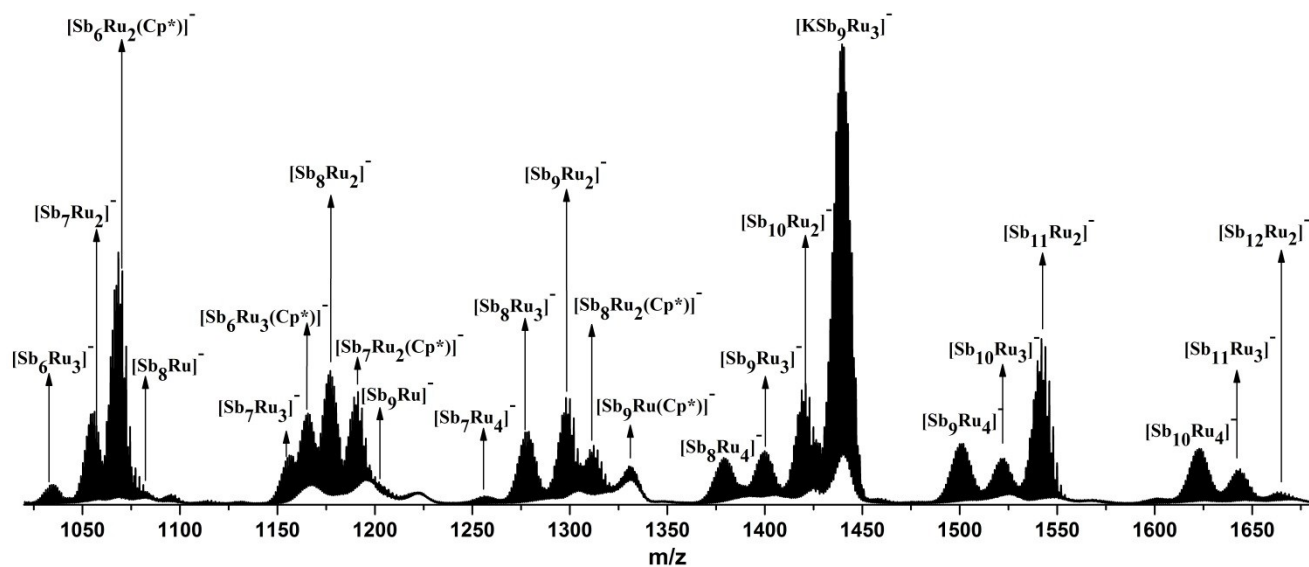
Fig S6 LDI-TOF mass spectrum of $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2]\cdot 2tol$ in negative-ion model.
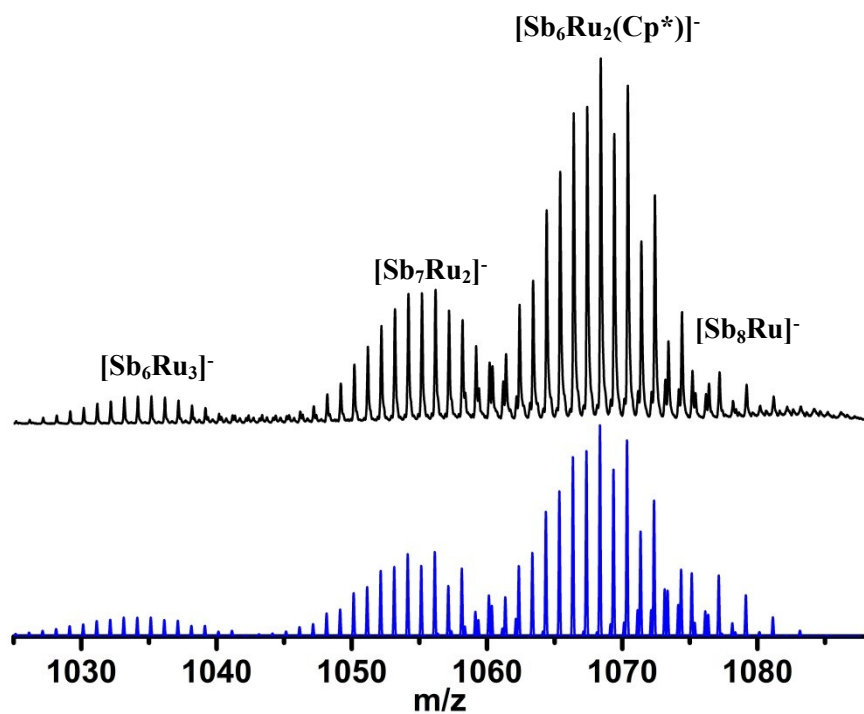

Fig S7 Comparison of experimental (top) and simulated (bottom) mass spectra of $[Sb_6Ru_3]^-$, $[Sb_7Ru_2]^-$, $[Sb_6Ru_2(Cp^*)]^-$ and $[Sb_8Ru]^-$ ions.
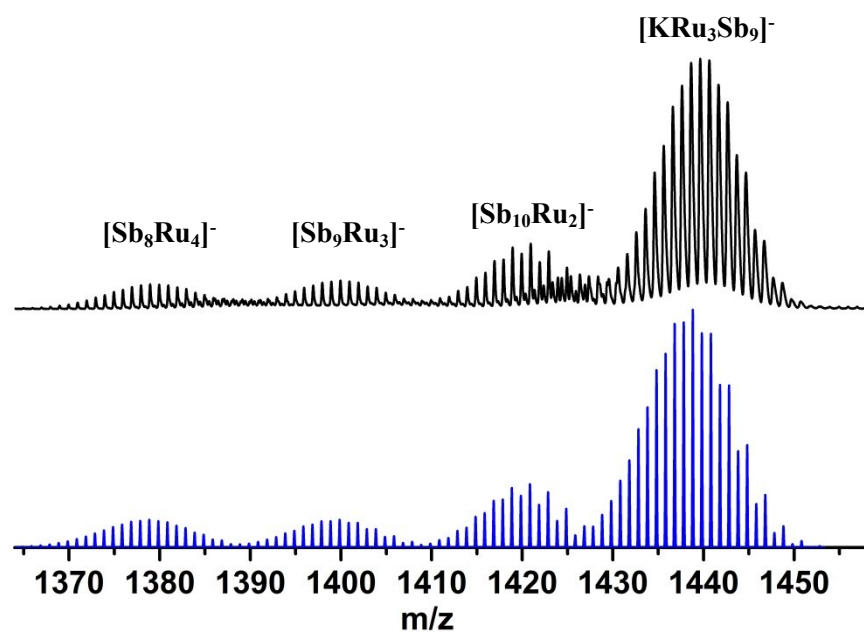
Fig S8 Comparison of experimental (top) and simulated (bottom) mass spectra of [Sb$_8$Ru$_4$]$^-$, [Sb$_9$Ru$_3$]$^-$, [Sb$_{10}$Ru$_2$]$^-$ and [KRu$_3$b$_9$]$^-$ ions.
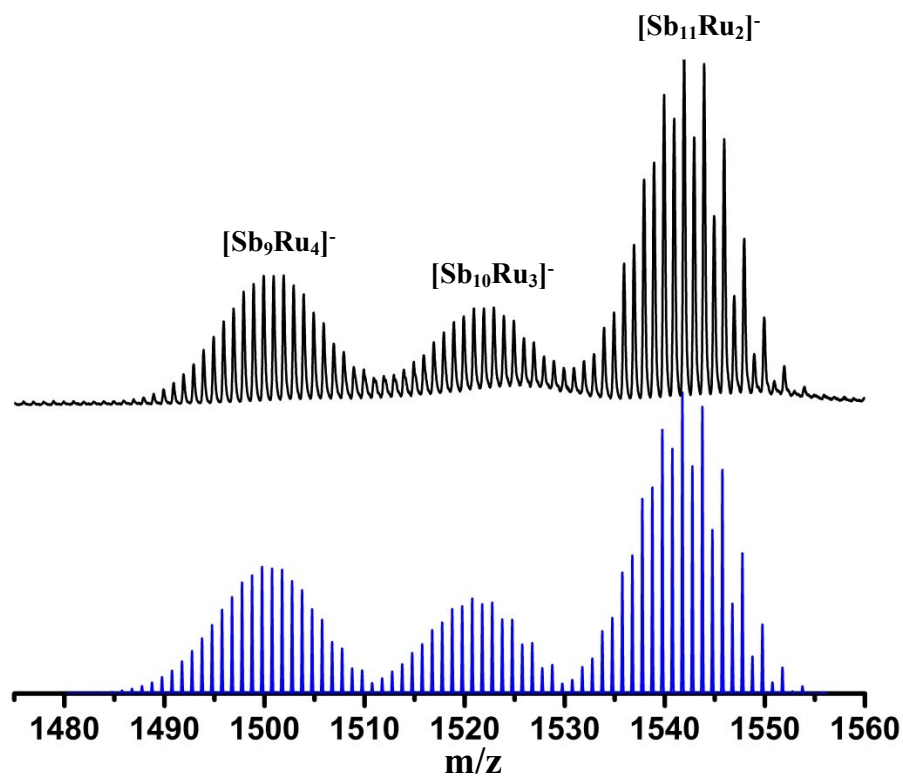
Fig S9 Comparison of experimental (top) and simulated (bottom) mass spectra of **[**Sb$_9$Ru$_4$]$^-$, [Sb$_{10}$Ru$_3$]$^-$ and [Sb$_{11}$Ru$_2$]$^-$ ions..