Synthesis, Structure and Bonding in Pentagonal Bipyramidal Cluster Compounds Containing a *cyclo*-Sn_5 Ring, $[(CO)_3MSn_5M(CO)_3]^{4-}$ (M = Cr, Mo).

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Section S1: Supplementary Crystallographic information

Figure S1. Crystals of $K_2(en)_3[K([2.2.2]\text{-crypt})]_2[Sn_5\{Cr(CO)_3\}_2]\cdot(en)_2$ (**1**, left) and $K[K(18\text{-crown-}6)]_3[Sn_5\{Mo(CO)_3\}_2$ (**2**, right) scattered on the filter paper, respectively.

Table S1. X-ray measurements and structure solution of $K_2(en)_3[K([2.2.2]\text{-crypt})]_2[Sn_5\{Cr(CO)_3\}_2]\cdot(en)_2$ (**1**) and $K[K(18\text{-crown-}6)]_3[Sn_5\{Mo(CO)_3\}_2$ (**2**)

Compound	**1**	**2**
CCDC number	2122111	2122112
Empirical formula	$C_{51}H_{106}N_{13}O_{18}K_4Cr_2Sn_5$	$C_{42}H_{72}O_{24}K_4Mo_2Sn_5$
Formula weight	2043.33	1902.72
Temperature/K	100.01(10)	100.00(10)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	16.0613(2)	24.1911(2)
b/Å	16.5096(2)	15.80710(10)
c/Å	18.0141(2)	20.20680(10)
α/°	107.1010(10)	90
β/°	93.6440(10)	102.4720(10)
γ/°	112.5370(10)	90
Volume/Å^3	4131.96(9)	7544.56(9)
Z	2	4
ρ_{calc}g/cm^3	1.642	1.675
μ/mm^{-1}	16.243	18.075
F(000)	2042	3704
2Θ range for data collection/°	7.83 to 133.984	7.166 to 133.99
Reflections collected	41350	46710
Data/restraints/parameters	14688/3105/885	13436/0/694
Goodness-of-fit on F^2	1.031	1.045
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0552, wR_2 = 0.1407	R_1 = 0.0414, wR_2 = 0.1147
Final *R* indexes [all data]	R_1 = 0.0583, wR_2 = 0.1429	R_1 = 0.0459, wR_2 = 0.1175
Largest diff. peak/hole / e Å^{-3}	2.00/-2.57	2.13/-1.21

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$
[b] GooF = $\{\sum w[(Fo)^2-(Fc)^2]^2/(n-p)\}^{1/2}$

Table S2. Geometrical parameters including bond lengths [Å] and angles [°] for $[Sn_5\{M(CO)_3\}_2]^{4-}$ cluster anions and Sn_5-containing anions in known Zintl phases Na_8BaSn_6 and Na_8EuSn_6.

Types	bond	1-Cr	2-Mo	Na_8EuSn_6	Na_8BaSn_6
Distances (Å)	Sn1-Sn2	2.892(3)	2.9382(5)	2.876(2)	2.911(1)
	Sn2-Sn3	2.899(3)	2.9202(5)	2.894(2)	2.939(1)
	Sn3-Sn4	2.872(4)	2.9225(4)	2.864(2)	2.894(1)
	Sn4-Sn5	2.909(4)	2.9328(5)	2.878(2)	2.915(1)
	Sn5-Sn1	2.744(3)	2.9542(5)	2.907(2)	2.916(1)
	M1/2-Sn1	2.871(3)	2.9335(5)	—	—
	M1/2-Sn2	2.863(3)	2.9602(5)	—	—
	M1/2-Sn3	2.809(3)	2.9653(5)	—	—
	M1/2-Sn4	2.841(4)	2.9314(5)	—	—
	M1/2-Sn5	2.868(9)	2.9481(5)	—	—
Angles (°)	Sn1-Sn2-	106.43(11)	107.974(13)	108.37(7)	108.74(5)
	Sn2-Sn3-	108.35(14)	107.917(13)	107.91(7)	107.73(5)
	Sn3-Sn4-	106.81(15)	108.970(13)	108.32(7)	108.28(5)
	Sn4-Sn5-	108.86(9)	106.827(13)	108.05(7)	108.42(5)
	Sn5-Sn1-	109.45(10)	108.240(13)	107.35(7)	106.83(5)

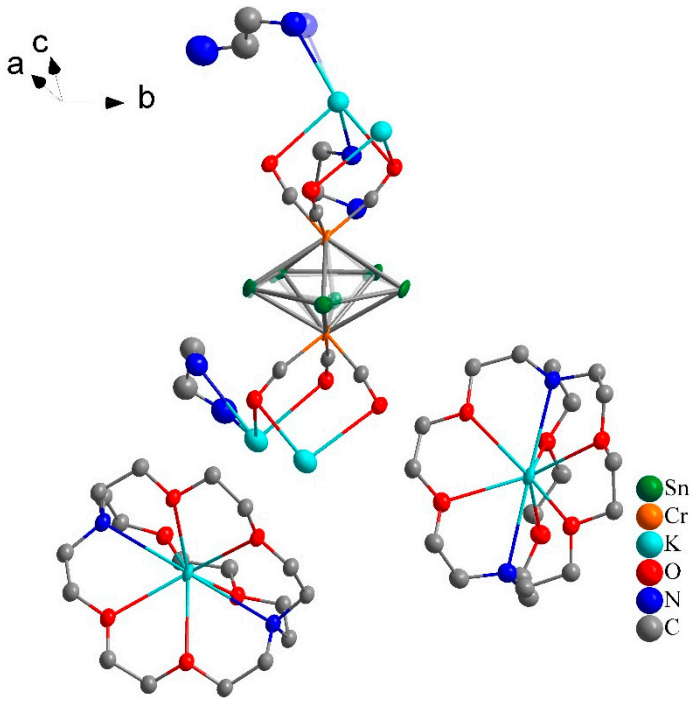

Figure S2. Asymmetric unit of **1** with the cluster fragment. Thermal ellipsoids are drawn at 50% probability. The second component of the disordered anion is shown as 50% transparent.

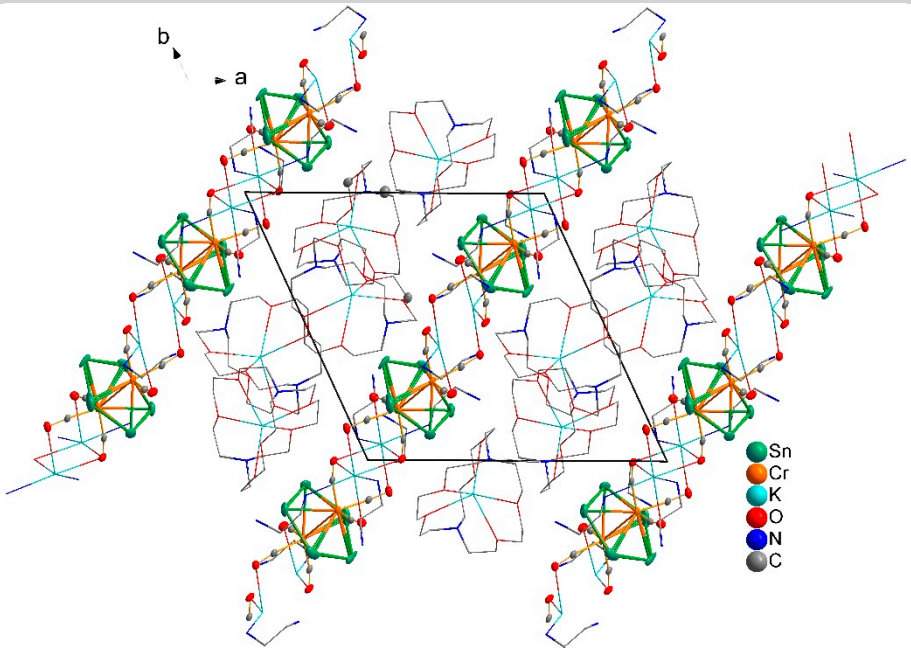

Figure S3. Unit cell of **1**. Thermal ellipsoids are drawn at 50% probability. Minor component in the cluster site are omitted for clarity.

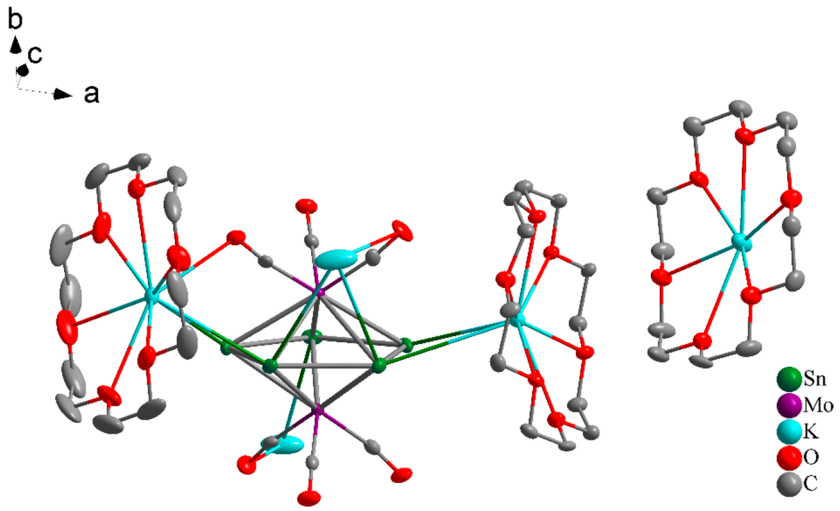

Figure S4. Asymmetric unit of **2** with the cluster fragment. Thermal ellipsoids are drawn at 50% probability.

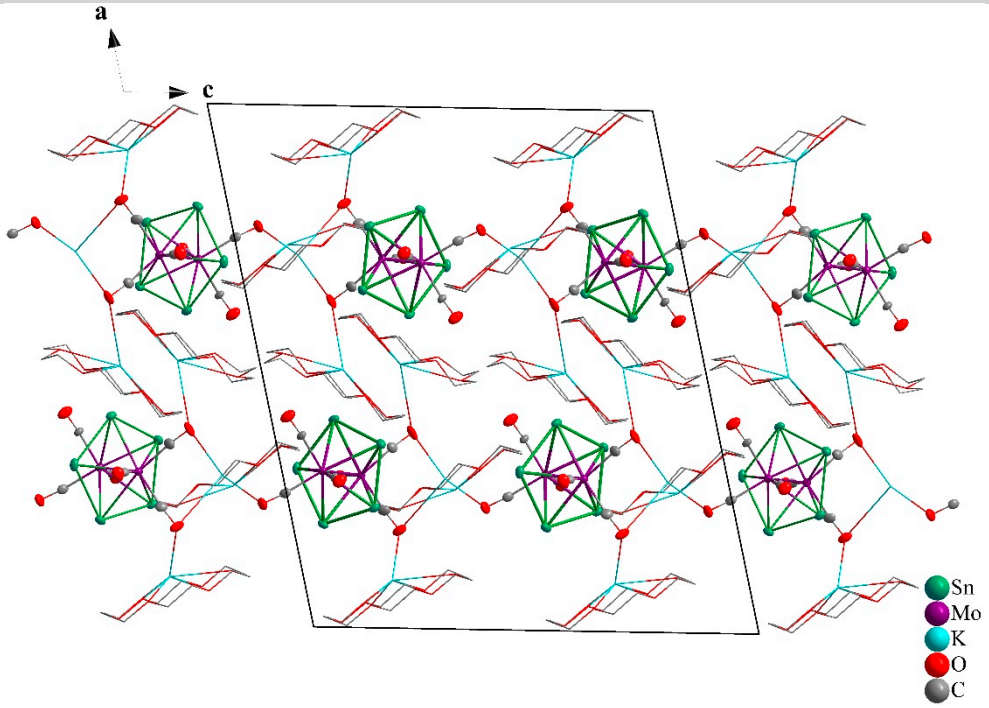

Figure S5. Unit cell of **2**. Thermal ellipsoids are drawn at 50% probability.

Section S2: ESI-MS Studies

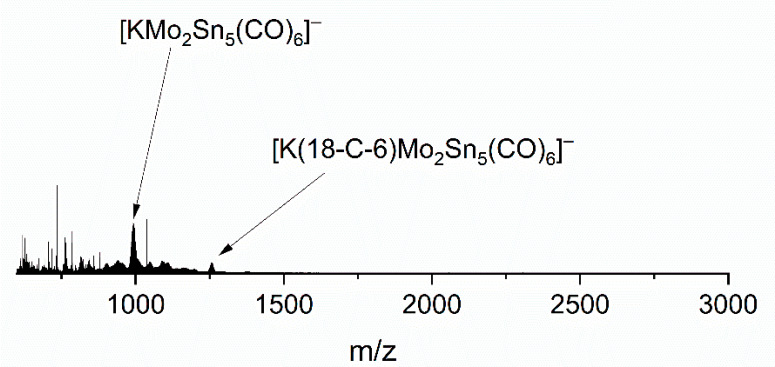

Figure S6. Overview ESI mass spectrum in negative ion mode of a freshly dissolved crystalline sample of **2** in MeCN.

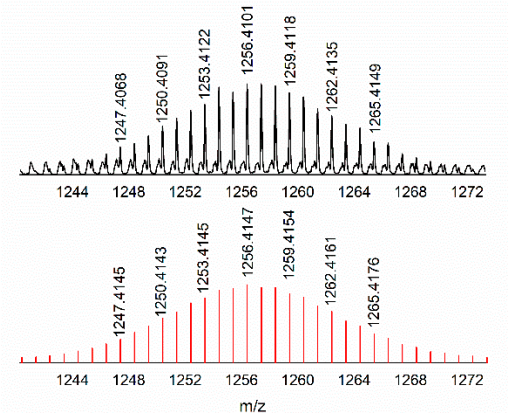

Figure S7. Measured (top) and simulated (bottom) spectrum of the fragment [K(18-C-6)$Mo_2Sn_5(CO)_6$]$^-$.

Section S3: Energy Dispersive X-ray (EDX) Spectroscopic Analysis

EDX analysis on **1** and **2** (Figures S12 and S13) was performed by a scanning electron microscope (FE-SEM, JEOL JSM-7800F, Japan). Data acquisition was performed with an acceleration voltage of 15 kV and an accumulation time of 60 s. Multiple crystals were used for EDX spectroscopic analysis, and data were recorded: different positions on one single crystal and different positions on other single crystals.

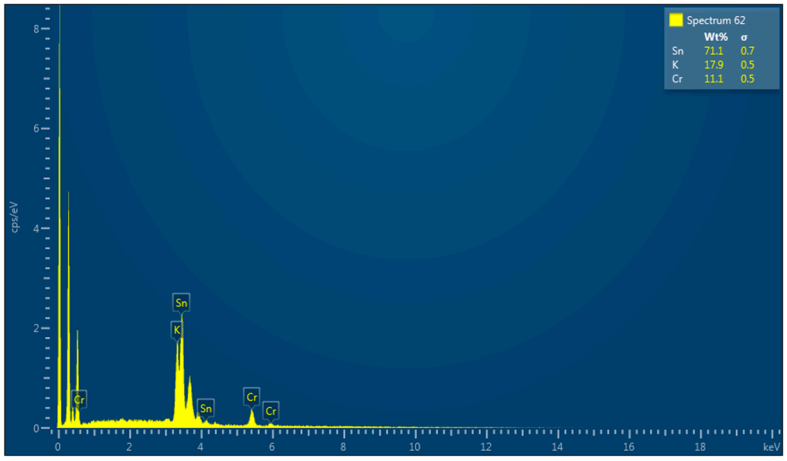

Figure S8. EDX analysis of **1**.

Element	Line type	wt%	σ	Experimental /
K	K series	17.9	0.5	3.8/4
Cr	L series	11.1	0.5	1.8/2
Sn	L series	71.1	0.7	5/5

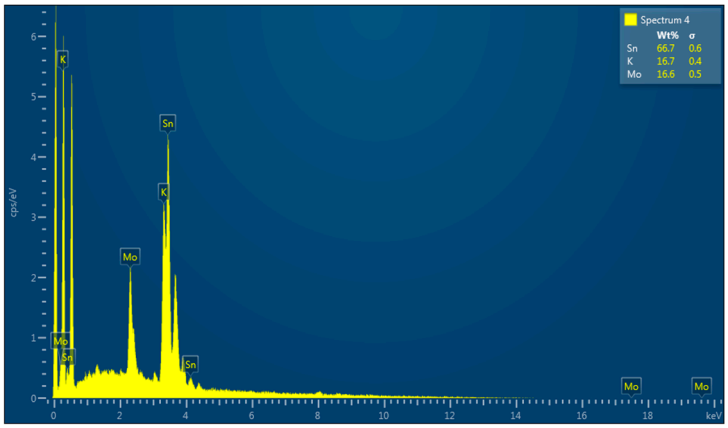

Figure S9. EDX analysis of **2**.

Element	Line type	wt%	σ	Experimental /
K	K series	16.7	0.4	4.1/4
Mo	L series	16.6	0.5	1.7/2
Sn	L series	66.7	0.6	5.4/5

Section S4: Quantum Chemical Analysis

All the calculations are performed as described in the experimental section. Optimised cartesian co-ordinates (in Å) for all reported complexes for PBE functionals are summarized below:

$[(CO)_3CrSn_5Cr(CO)_3]^{4-}$

Sn	4.737018000	2.980643000	2.212367000
Sn	3.668424000	-1.341625000	3.764593000
Cr	2.576263000	1.070303000	2.594900000
Cr	4.903195000	1.195278000	4.448793000
O	1.749589000	2.892443000	0.366565000
O	1.779630000	-1.093420000	0.678749000
O	5.629236000	-0.612430000	6.727349000
O	5.754723000	3.324244000	6.373840000
O	7.836564000	1.264766000	3.839620000
C	0.840485000	1.213713000	3.074688000
C	2.192051000	2.234917000	1.267454000
C	2.191761000	-0.299196000	1.482605000
C	5.246172000	0.034429000	5.788684000
C	5.305636000	2.547212000	5.577181000
C	6.642031000	1.210898000	3.959818000
Sn	5.172424000	0.136377000	1.752244000
Sn	2.851177000	3.258572000	4.423754000
Sn	2.279930000	0.585600000	5.450558000
O	-0.351712000	1.317783000	3.181456000

$[(CO)_3MoSn_5Mo(CO)_3]^{4-}$

Sn	8.121766000	10.456199000	13.142953000
Sn	5.185549000	10.557560000	12.628846000
Sn	9.485306000	12.067251000	11.037825000
Sn	4.723426000	12.250861000	10.211485000
Sn	7.387155000	13.161850000	9.208703000
Mo	6.865327000	13.005689000	12.159844000
Mo	7.087693000	10.401720000	10.322907000
O	4.440529000	13.875120000	13.954710000
O	5.348481000	9.585341000	7.842802000
O	8.825600000	13.893727000	14.446276000
O	9.426085000	9.567251000	8.403426000
O	6.890149000	7.410697000	11.259817000
C	5.321445000	13.457325000	13.263978000
C	8.598588000	9.953999000	9.172823000
C	6.866900000	14.856789000	11.541972000
C	8.125680000	13.477550000	13.570374000
C	5.941136000	9.970122000	8.804972000
C	6.956439000	8.573964000	10.988908000
O	6.833290000	16.029264000	11.322160000

$[(CO)_3\,MoPb_5\,Mo(CO)_3]^{4-}$

Pb	0.421489000	2.580258000	0.028521000
Pb	-2.346011000	1.164861000	-0.022120000
Pb	-1.851777000	-1.899092000	0.029705000
Pb	1.211059000	-2.361378000	-0.010907000
Pb	2.625755000	0.387455000	-0.031437000
Mo	0.005719000	-0.010836000	-1.617028000
Mo	0.009182000	-0.015933000	1.611290000
C	-1.508928000	-0.542072000	-2.717192000
O	-2.351286000	-0.810167000	-3.527877000
C	1.276262000	-0.971809000	-2.734747000
O	1.992166000	-1.481437000	-3.551328000
C	0.232818000	1.541274000	-2.768879000
O	0.347540000	2.379250000	-3.615971000
C	-1.392697000	0.671377000	2.771863000
O	-2.147173000	1.042983000	3.623453000
C	0.068051000	-1.603169000	2.735378000
O	0.073431000	-2.476774000	3.556937000

C	1.314427000	0.931701000	2.699948000
O	2.019971000	1.473509000	3.505146000

$[CpCrP_5CrCp]^-$

Cr	2.698406000	1.059899000	2.725138000
Cr	4.745163000	1.172807000	4.367939000
P	4.240731000	-0.681463000	3.020300000
P	2.866328000	-0.207143000	4.708973000
P	4.904895000	1.336806000	2.059726000
P	3.930365000	3.044076000	3.157044000
P	2.665952000	2.099445000	4.789247000
C	6.510525000	0.133320000	5.161951000
C	6.925947000	1.360234000	4.560805000
C	6.303208000	2.430774000	5.271460000
C	5.501987000	1.867293000	6.310001000
C	5.631316000	0.446765000	6.242505000
H	6.808923000	-0.863608000	4.850434000
H	7.597970000	1.461797000	3.713473000
H	6.414489000	3.489458000	5.054781000
H	4.900598000	2.420823000	7.025469000
H	5.141062000	-0.270754000	6.894292000
C	2.024893000	1.093163000	0.634383000
C	1.396723000	2.163225000	1.340972000
C	0.596668000	1.599017000	2.380163000
C	0.728406000	0.178678000	2.313464000
C	1.611035000	-0.134173000	1.235752000
H	2.698738000	1.195068000	-0.211520000
H	1.514162000	3.222304000	1.129732000
H	-0.006424000	2.152142000	3.094450000
H	0.246377000	-0.538758000	2.971439000
H	1.914912000	-1.130571000	0.927901000

Tl_7^{7-}

Tl	-0.376180000	1.633978000	-2.282422000
Tl	0.360685000	-1.586372000	-2.324641000
Tl	0.781438000	-2.593996000	0.850333000
Tl	-0.004273000	-0.022027000	2.829864000
Tl	-0.772621000	2.579006000	0.889767000
Tl	-1.592381000	-0.462413000	0.025215000
Tl	1.603332000	0.451825000	0.011885000

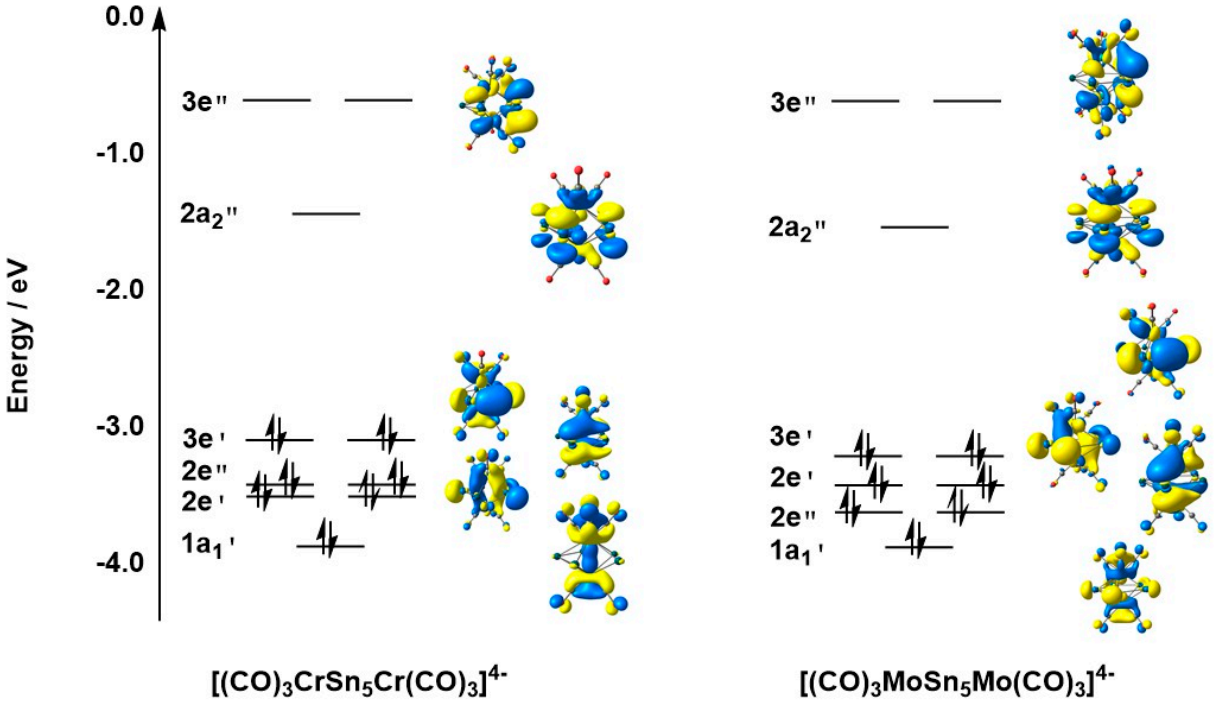

Figure S10. Kohn-Sham molecular orbital diagrams for $[(CO)_3CrSn_5Cr(CO)_3]^{4-}$ and $[(CO)_3MoSn_5Mo(CO)_3]^{4-}$.