Supporting Information

Solvothermal Synthesis, Structure and Physical Properties of $Cs[Cr(en)_2MSe_4]$ (M = Ge, Sn) with $[MSe_4]^{4-}$ Tetrahedra as Chelating Ligand

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Table S1. Selected Bond Distances (Å) and Angles for $Cs[Cr(en)_2MSe_4]$

parameter	*M* = Ge	parameter	*M* = Sn
Cr1-N1	2.093(6)	Cr1-N1	2.091(4)
Cr1-N2	2.084(6)	Cr1-N2	2.076(5)
Cr1-N3	2.103(7)	Cr1-N3	2.112(4)
Cr1-N4	2.081(6)	Cr1-N4	2.083(5)
Cr1-Se1	2.495(1)	Cr1-Se1	2.518(1)
Cr1-Se2	2.520(1)	Cr1-Se2	2.535(1)
Ge1-Se1	2.379(1)	Sn1-Se1	2.5518(7)
Ge1-Se2	2.371(1)	Sn1-Se2	2.5340(7)
Ge1-Se3	2.319(1)	Sn1-Se3	2.5012(7)
Ge1-Se4	2.327(1)	Sn1-Se4	2.4891(7)
Cs1-Se1	3.5053(9)	Cs1-Se3	3.5506(7)
Cs1-Se2	3.5902(9)	Cs1-Se2	3.6290(7)
Cs1-Se4	3.598(1)	Cs1-Se3	3.6675(7)
Cs1-Se3	3.6228(9)	Cs1-Se1	3.7196(7)
Cs1-Se4	3.8404(8)	Cs1-Se4	3.7436(7)
Cs1-Se2	3.964(1)	Cs1-Se1	3.8181(8)
Cr1- Ge1	3.311(1)	Cr1- Sn1	3.4746(9)
Cr1-Cr1	6.065(2)	Cr1-Cr1	6.542(1)

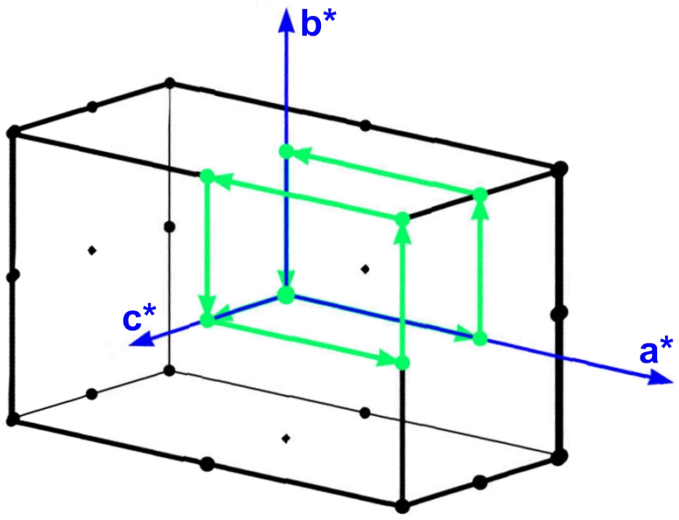

Figure S1. The Brillouin zone and k-space pathway for $Cs[Cr(en)_2SnSe_4]$

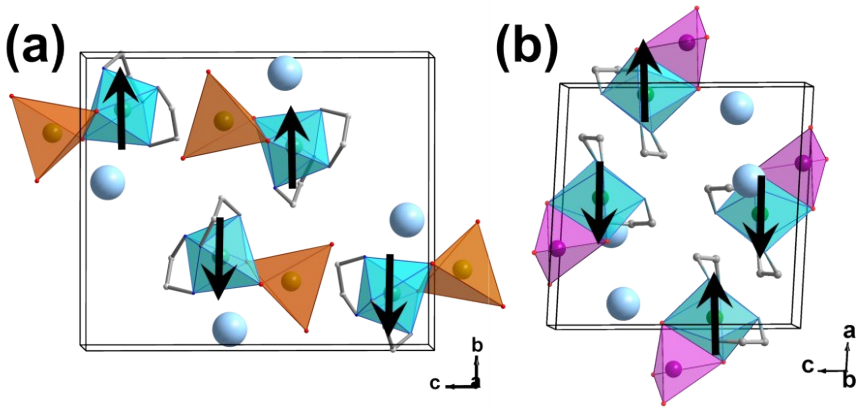

Figure S2. Schematic representations of the AFM models for the compound (a) $Cs[Cr(en)_2SnSe_4]$ and (b) $Cs[Cr(en)_2GeSe_4]$. (↑: spin-up, ↓: spin-down).

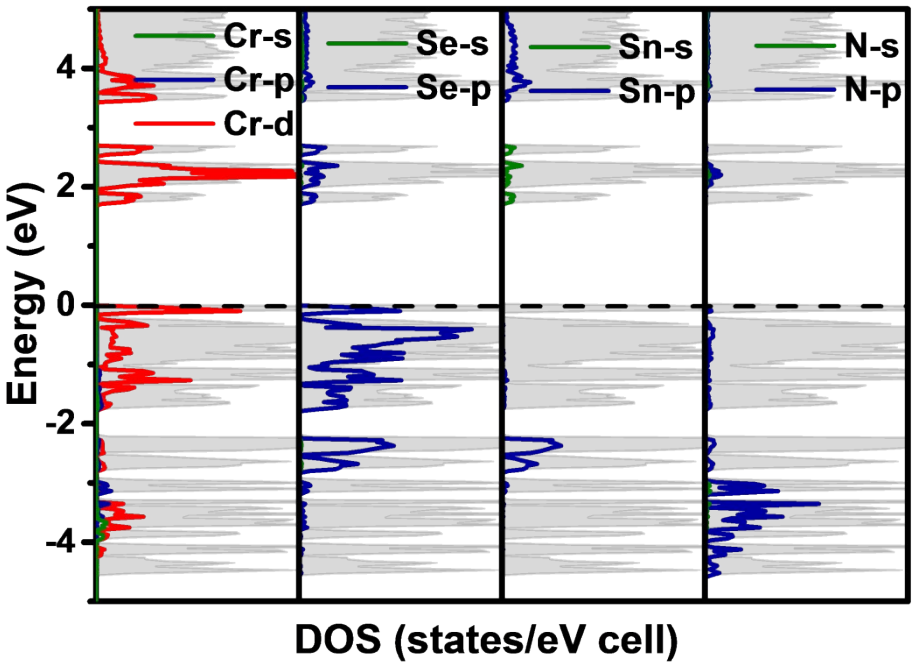

Figure S3. Partial Dos of $Cs[Cr(en)_2SnSe_4]$

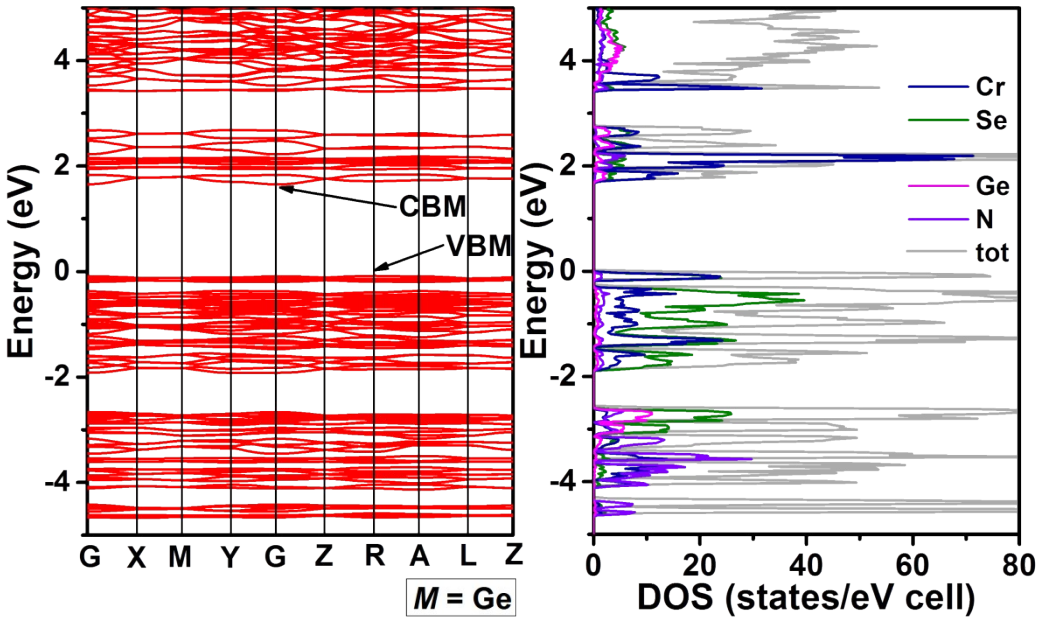

Figure S4. Calculated local electronic band structure (left) and partial density of states (right) for $Cs[Cr(en)_2GeSe_4]$. (G (0, 0, 0), X (1/2, 0, 0), M (1/2, 1/2, 0), Y (0, 1/2, 0), Z (0, 0, 1/2), R (1/2, 0, 1/2), A (1/2, 1/2, 1/2), L (0, 1/2, 1/2))

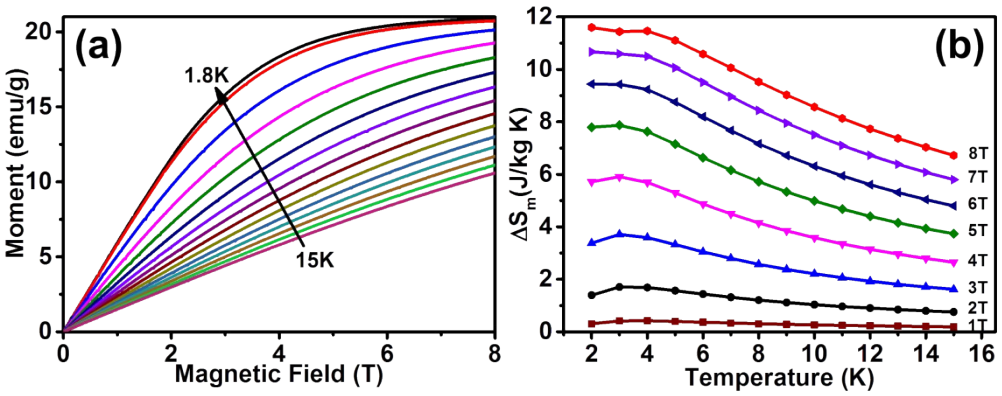

Figure S5. Magnetization *vs*. field for **1** in the temperature range of 1.8–8.2 K. (a) Field-dependent magnetization plots for $Cs[Cr(en)_2GeSe_4]$ at 1.8K, 2K, 3K, 4K, 5K, 6K, 7K, 8K, 9K, 10K, 11K, 12K, 13K, 14K, and 15K. (b) ΔS_m calculated by using the magnetization data of $Cs[Cr(en)_2GeSe_4]$ at different fields and temperatures.

Table S2. Magnetic Entropy Change for Selected 3*d*-metal Molecule-Based Magnetic Coolants reported recently

Compound	$-\Delta S_m$ [J/kg K]	$-\Delta S_m$ [mJ/cm^3 K]	T [K]	$\mu_0\Delta H$ [T]	Density [g/cm^3]	Ref
$Cs[Cr(en)_2SnSe_4]$ (this work)	14.2	44.0	2.0	8	3.099	
$Cs[Cr(en)_2GeSe_4]$ (this work)	11.6	33.4	2.0	8	2.884	
$Mn^{II}_4(N_3)_{7.3}Cl_{0.7}(dafo)_4$	19.3	33.3	4.0	5	1.722	1
$Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6$	17.6	34.0	6.0	7	1.933	2
$[Mn_{10}(OH)_6(amp)_4(ampH)_4I_4(EtOH)_4]I_4\cdot 12EtOH$	17.0	26.2	5.2	7	1.543	3
$[Mn_{14}(OH)_2(Hpeol)_4(H_2peol)_6I_4(EtOH)_6]I_4$	25.0	42.5	3.8	7	1.700	3
$Fe_{14}O_6(C_2H_2N_3)_6(OMe)_{18}Cl_6$	20.3	37	6.0	7	1.782	4
$[Mn(bpy)_3]_{1.5}[Mn_{32}(thme)_{16}(bpy)_{24}(N_3)_{12}(OAc)_{12}](ClO_4)_{11}$	18.2	25	1.6	7	1.4	5
$[Fe_{14}(C_2H_2N_3)_6O_6(OMe)_{18}Cl_6]\cdot 4.5MeOH$	20.3	42.2	6.0	7	2.079	6
$Mn(glc)_2$	6.9	13.1	7.0	7	1.898	7
$Mn(glc)_2(H_2O)_2$	60.3	112	1.8	7	1.857	7
Mn(Me-ip)(DMF)	42.4	66.7	3.0	8	1.572	8
$Cs_2NaAl_{0.38}Cr_{0.62}F_6$	16.6	71.7	3.0	10	4.32	9
$[CH_3NH_2CH_3][CrMn(HCOO)_6]$	43.9	74.7	3.0	7	1.702	10
$[CH_3NH_3][CrMn(HCOO)_6]$	48.2	78.5	3.0	7	1.628	10

Reference:

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