Table S1 Fractional coordinates of the optimized structures of $Ca_3Co_2O_6$ from LDA+U+SOC (VASP) calculations with U_{eff} (Co) = 4 eV (see the text)

	with C_3 rotational symmetry			without C_3 rotational symmetry		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Ca	0.88338	0.24984	0.61652	0.88300	0.25272	0.61727
Ca	0.61659	0.88345	0.25017	0.61681	0.88201	0.24914
Ca	0.25000	0.61669	0.88337	0.24853	0.61571	0.88492
Ca	0.11661	0.75019	0.38345	0.11668	0.74813	0.38281
Ca	0.38342	0.11648	0.74988	0.38202	0.11709	0.75211
Ca	0.74993	0.38333	0.11671	0.75013	0.38492	0.11636
Co	0.00000	-0.00004	0.00004	0.00067	-0.00080	0.00004
Co	0.50005	0.50003	0.49991	0.50035	0.50044	0.49904
Co	0.24978	0.25034	0.24989	0.24864	0.24796	0.25344
Co	0.74991	0.74975	0.75034	0.74711	0.75317	0.74983
O	0.96239	0.08917	0.28769	0.96452	0.09394	0.28732
O	0.28779	0.96260	0.08937	0.28828	0.96133	0.08972
O	0.08946	0.28775	0.96271	0.09298	0.28618	0.96173
O	0.41075	0.53752	0.21221	0.40845	0.53862	0.21242
O	0.53751	0.21224	0.41073	0.53529	0.21297	0.40544
O	0.21232	0.41051	0.53725	0.21276	0.40904	0.53858
O	0.03757	0.91078	0.71226	0.03564	0.90528	0.71280
O	0.71228	0.03729	0.91049	0.71289	0.03707	0.90808
O	0.91073	0.71223	0.03742	0.90962	0.71271	0.04022
O	0.58942	0.46267	0.78774	0.59447	0.46354	0.78615
O	0.46238	0.78777	0.58919	0.46348	0.78772	0.59208
O	0.78773	0.58940	0.46266	0.78767	0.59023	0.46050

$Ca_3Co_2O_6$

space group *R-3c*, a = b = 9.0793 Å, c = 10.381 Å

α = β = 90º, γ = 120º

Table S2 Fractional coordinates of the optimized structures of Ca_3CoRhO_6 from LDA+U+SOC (VASP) calculations with U_{eff} (Co) = 4 eV and U_{eff} (Rh) = 2 eV (see the text)

	with C_3 rotational symmetry			without C_3 rotational symmetry		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Ca	0.88869	0.61131	0.24987	0.88945	0.61082	0.24619
Ca	0.11133	0.38868	0.75008	0.11049	0.38918	0.75391
Ca	0.61135	0.25012	0.88866	0.61026	0.25357	0.88931
Ca	0.38867	0.74985	0.11131	0.38968	0.74656	0.11067
Ca	0.25002	0.88860	0.61138	0.25024	0.88659	0.61358
Ca	0.75007	0.11138	0.38860	0.74944	0.11350	0.38650
Co	0.25009	0.24975	0.25008	0.24904	0.24358	0.25727
Co	0.75003	0.75015	0.74978	0.75024	0.75678	0.74300
Rh	-0.00001	0.00002	0.00002	0.00007	0.00000	-0.00008
Rh	0.49998	0.50000	0.50002	0.50007	0.49990	0.50005
O	0.95769	0.29509	0.09019	0.95243	0.29423	0.08629
O	0.04232	0.70488	0.90987	0.04767	0.70590	0.91350
O	0.29513	0.09032	0.95796	0.29497	0.09316	0.96059
O	0.70486	0.90972	0.04212	0.70512	0.90664	0.03919
O	0.45768	0.59017	0.79510	0.45260	0.58670	0.79408
O	0.54231	0.40988	0.20488	0.54748	0.41303	0.20602
O	0.09018	0.95783	0.29520	0.09010	0.96066	0.29644
O	0.90973	0.04210	0.70485	0.91025	0.03954	0.70345
O	0.59021	0.79520	0.45789	0.58957	0.79633	0.45990
O	0.40970	0.20485	0.54206	0.41076	0.20355	0.54029
O	0.79510	0.45793	0.59032	0.79515	0.46122	0.59335
O	0.20487	0.54216	0.40974	0.20491	0.53855	0.40649

Ca_3CoRhO_6

space group *R-3c*, a = b = 9.2017 Å, c = 10.7296 Å

α = β = 90º, γ = 120º

Table S3 Fractional coordinates of the optimized structures of Ca_3CoIrO_6 from LDA+U+SOC (VASP) calculations with U_{eff} (Co) = 4 eV and U_{eff} (Ir) = 2 eV (see the text)

	with C_3 rotational symmetry			without C_3 rotational symmetry		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Ca	0.38627	0.75000	0.11373	0.38656	0.74713	0.11322
Ca	0.61373	0.25000	0.88627	0.61344	0.25289	0.88679
Ca	0.75000	0.11373	0.38627	0.74975	0.11536	0.38457
Ca	0.25000	0.88627	0.61373	0.25020	0.88463	0.61542
Ca	0.88627	0.61373	0.25000	0.88641	0.61330	0.24692
Ca	0.11373	0.38627	0.75000	0.11358	0.38670	0.75311
Co	0.24999	0.25002	0.25000	0.24956	0.24467	0.25573
Co	0.74999	0.75000	0.75000	0.75028	0.75540	0.74434
Rh	0.00002	0.00000	-0.00002	0.00000	0.00001	-0.00002
Rh	0.50000	0.49999	0.50003	0.50002	0.49999	0.50000
O	0.70160	0.91062	0.04422	0.70160	0.90810	0.04143
O	0.29838	0.08937	0.95578	0.29844	0.09187	0.95853
O	0.91062	0.04422	0.70162	0.91113	0.04360	0.70059
O	0.08938	0.95578	0.29840	0.08894	0.95645	0.29937
O	0.20161	0.54422	0.41062	0.20147	0.54118	0.40808
O	0.79839	0.45578	0.58938	0.79856	0.45879	0.59191
O	0.04422	0.70161	0.91062	0.04762	0.70233	0.91265
O	0.95578	0.29839	0.08938	0.95239	0.29769	0.08730
O	0.54422	0.41061	0.20160	0.54736	0.41242	0.20238
O	0.45578	0.58938	0.79838	0.45265	0.58753	0.79765
O	0.41062	0.20161	0.54422	0.41138	0.20065	0.54398
O	0.58938	0.79839	0.45578	0.58867	0.79930	0.45604

Ca_3CoIrO_6

space group *R-3c*, a = b = 9.1811 Å, c = 10.8232 Å

α = β = 90º, γ = 120º

Table S4. Slater-type atomic orbital parameters used for extended Hückel tight binding calculations [a]

Atom	χ_i	H_{ii}(eV)	ζ_1	C_1	ζ_2'	C_2
V	4s	-8.81	1.697	1.0		
V	4p	-5.52	1.260	1.0		
V	3d	-11.0	5.052	0.3738	2.173	0.7456
O	2s	-32.3	2.88	0.7076	1.675	0.3745
O	2p	-14.8	3.694	0.3322	1.659	0.7448

[a] H_{ii}'s are the diagonal matrix elements $\langle \chi_i | H^{eff} | \chi_i \rangle$, where H^{eff} is the effective Hamiltonian. In our calculations of the off-diagonal matrix elements $H_{ij} = \langle \chi_i | H^{eff} | \chi_j \rangle$, the weighted formula was used. See: Ammeter, J.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R., *J. Am. Chem. Soc*. **1978**, *100*, 3686.

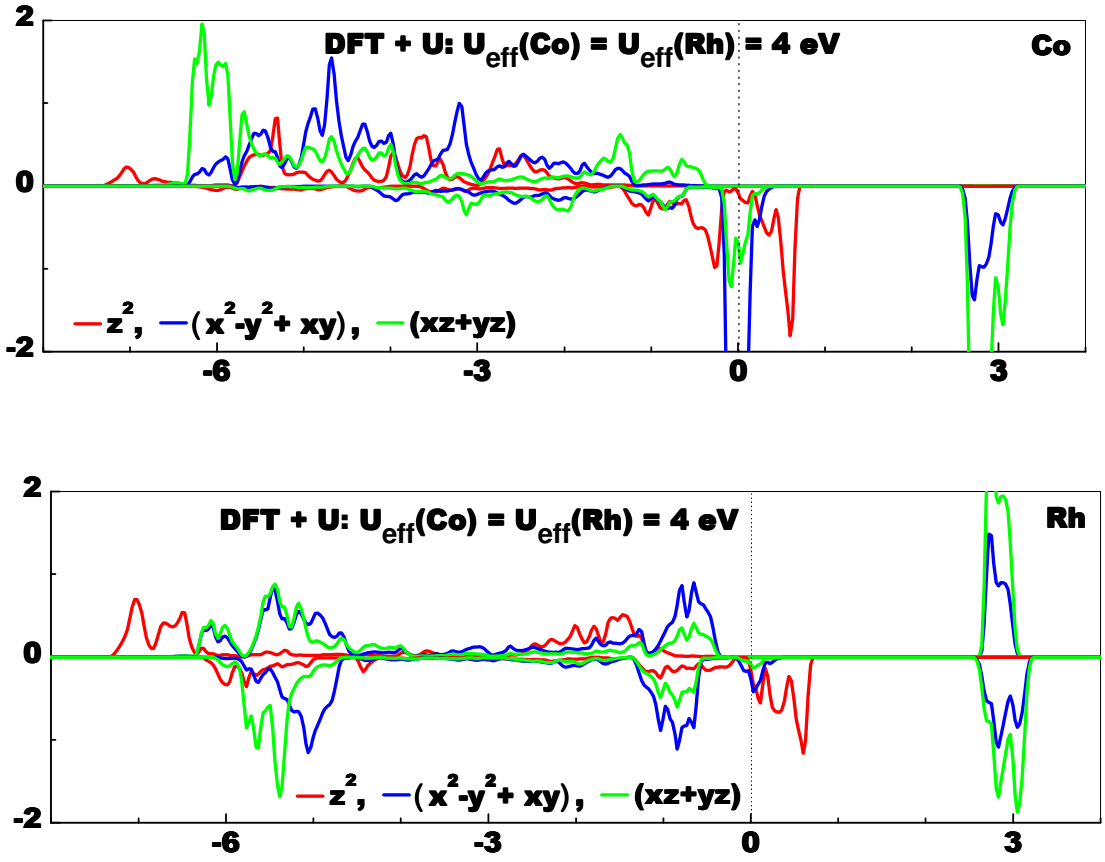

Figure S1. Projected DOS plots for the z^2, (x^2-y^2 + xy) and (xz + yz) states of the TP Co^{2+} and OCT Rh^{4+} ions in the FM state of Ca_3CoRhO_6 obtained from the LSDA+U calculations by using the FPLAPW method of the WIEN2k package, the experimental structure of Ca_3CoRhO_6, and $U_{eff}(Co) = U_{eff}(Rh) = 4$ eV.

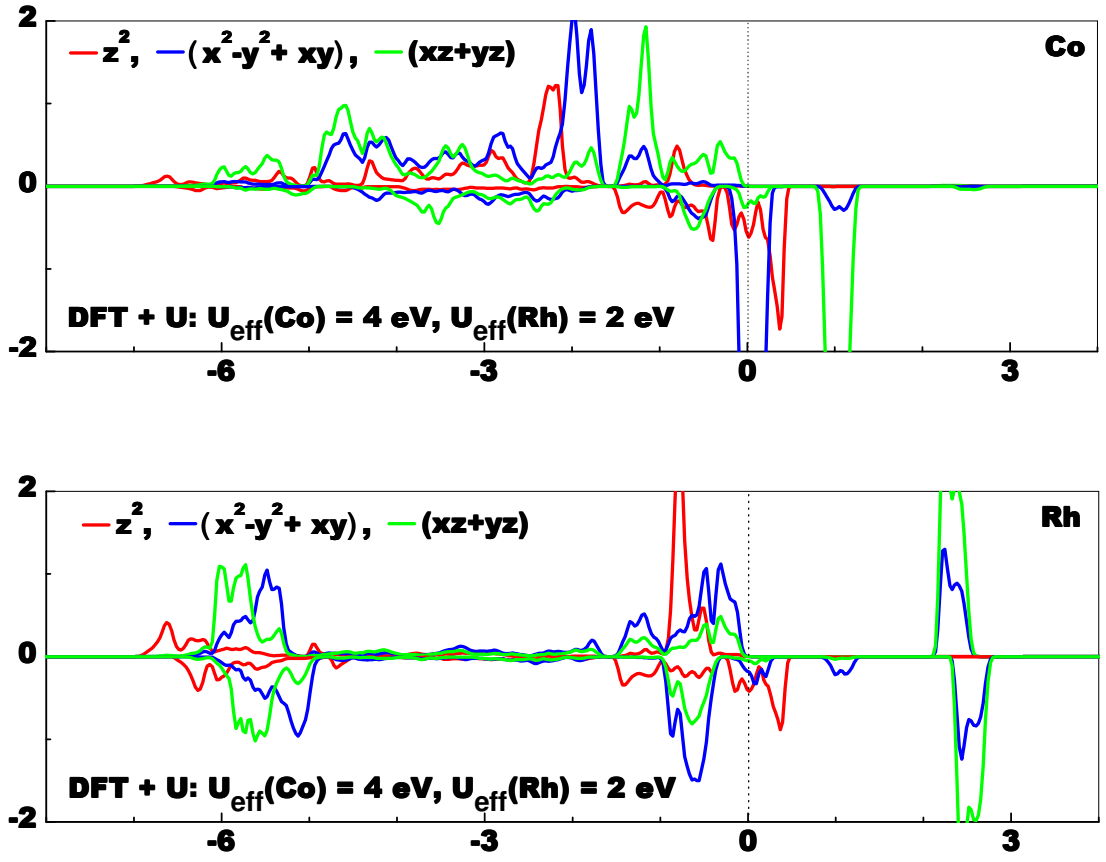

Figure S2. Projected DOS plots for the z^2, (x^2-y^2 + xy) and (xz + yz) states of the TP Co^{2+} and OCT Rh^{4+} ions in the FM state of Ca_3CoRhO_6 obtained from the LSDA+U calculations by using the FPLAPW method of the WIEN2k package, the experimental structure of Ca_3CoRhO_6, and U_{eff}(Co) = 4 eV and U_{eff}(Rh) = 2 eV.

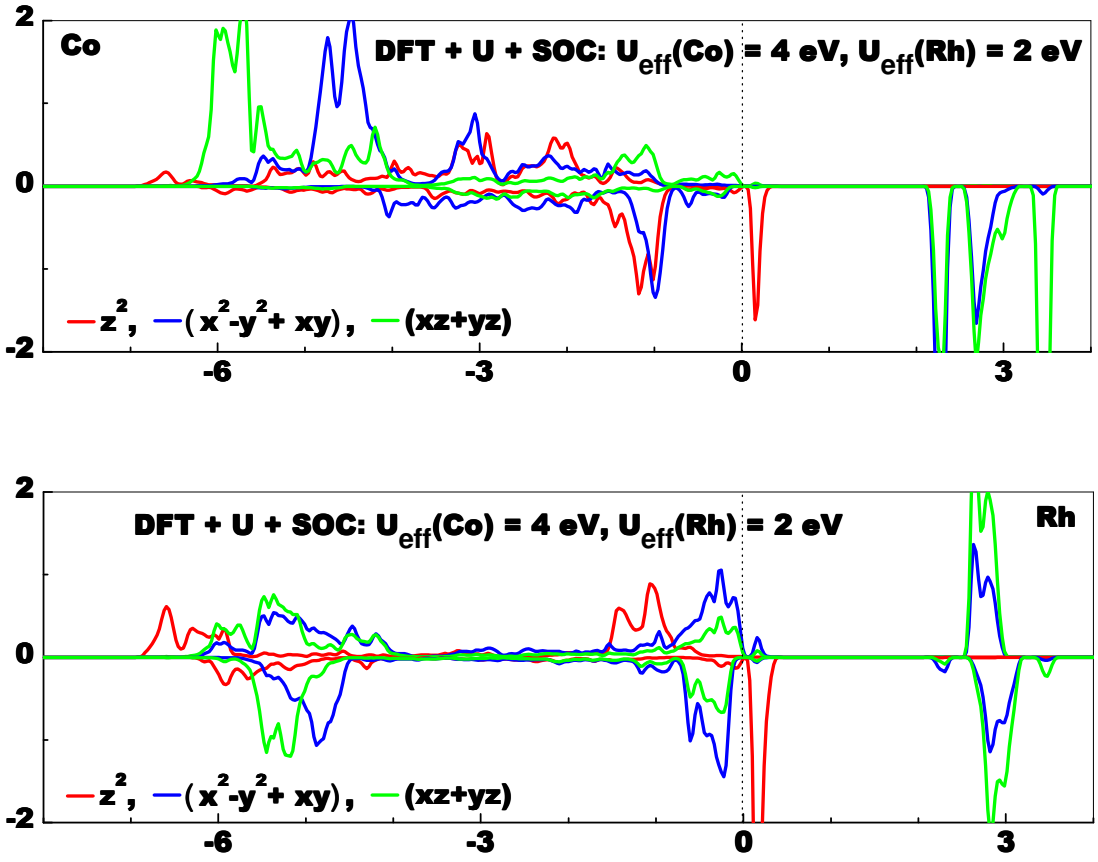

Figure S2. Projected DOS plots for the z^2, (x^2-y^2 + xy) and (xz + yz) states of the TP Co^{2+} and OCT Rh^{4+} ions in the FM state of Ca_3CoRhO_6 obtained from the LSDA+U+SOC calculations by using the FPLAPW method of the WIEN2k package, the experimental structure of Ca_3CoRhO_6, and U_{eff}(Co) = 4 eV and U_{eff}(Rh) = 2 eV.

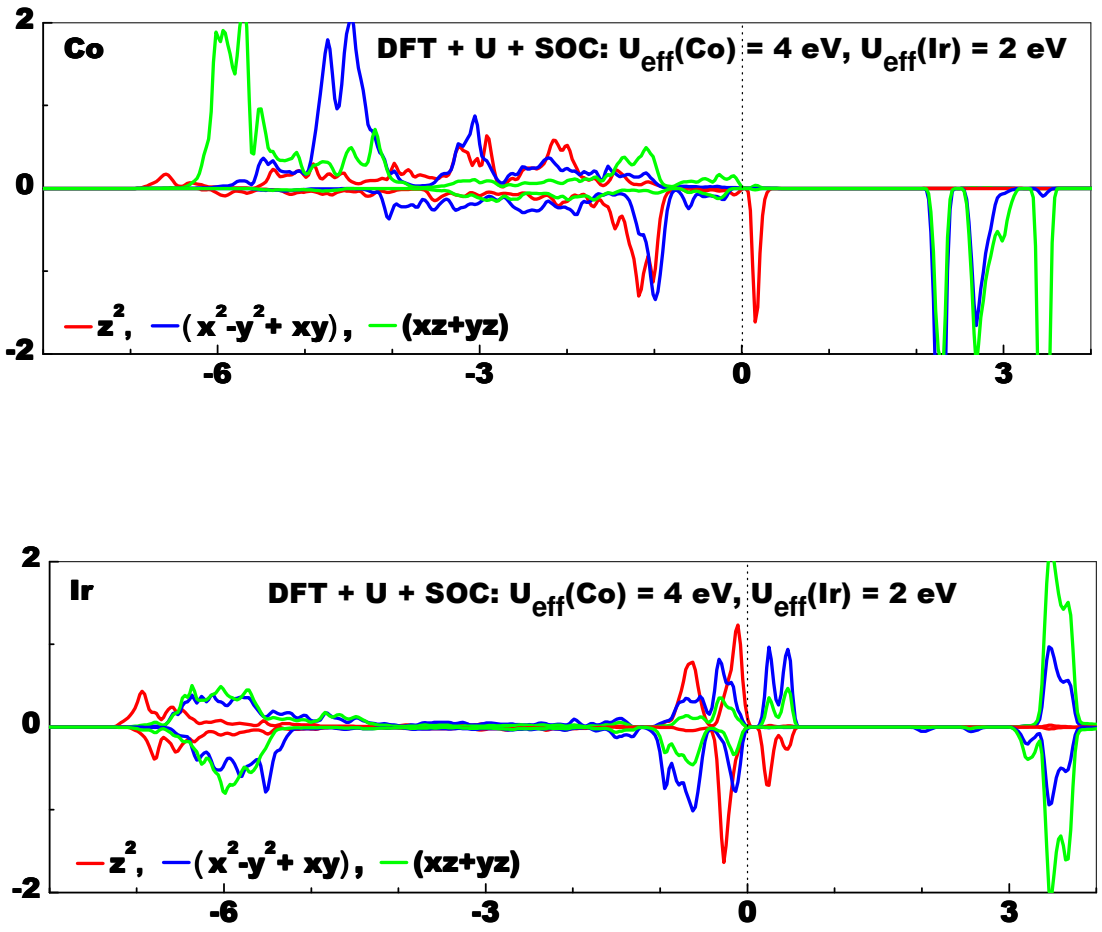

Figure S3. Projected DOS plots for the z^2, (x^2-y^2 + xy) and (xz + yz) states of the TP Co^{2+} and OCT Ir^{4+} ions in the FM state of Ca_3CoIrO_6 obtained from the LSDA+U and LSDA+U+SOC calculations by using the FPLAPW method of the WIEN2k package, the optimized structure of Ca_3CoIrO_6 with C_3 symmetry, and U_{eff}(Co) = 4 eV and U_{eff}(Ir) = 2 eV.