Supplementary Information

On the $CN^{-}\cdots K$ coordination modes in $K_n[M^{6-n}(CN)_6]\cdot xH_2O$: First evidence of $CN^{-}\cdots K$ electron-deficient bonding

Manuel Avila [a], Lucero Torres [a], Ana L. Montero-Alejo [b], Leslie Reguera *[a,c] and Edilso Reguera *[a]

a) Instituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, U. Legaria, Ciudad México, México; E-mail: edilso.reguera@gmail.com

b) Departamento de Física, Facultad de Ciencias Naturales, Matemática y del Medio Ambiente (FCNMM), Universidad Tecnológica Metropolitana, Santiago, Chile

c) Universidad de La Habana, Facultad de Química, La Habana, Cuba; E-mail: leslieregueraa2005@gmail.com

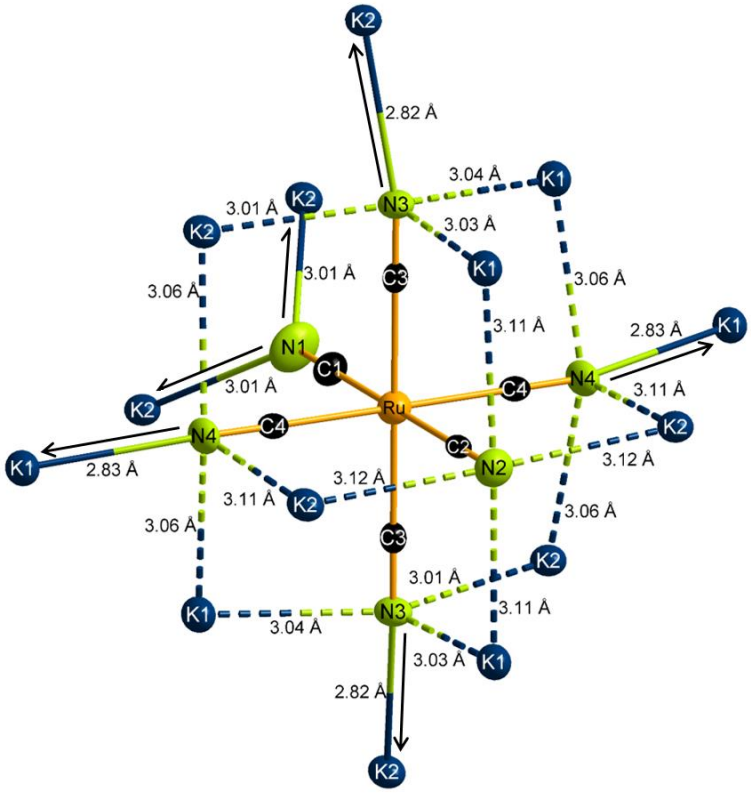


Figure S1. Network of interactions between K atoms and the N end of the CN ligands in $K_4[Ru(CN)_6]\cdot 3H_2O$

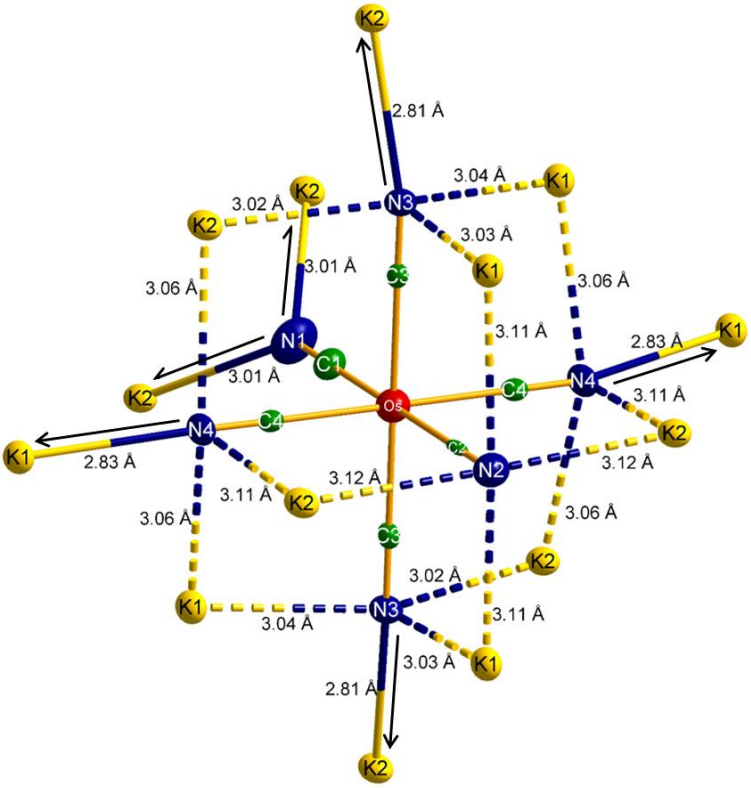


Figure S2. Network of interactions between K atoms and the N end of the CN^- ligands in $K_4[Os(CN)_6]\cdot 3H_2O$

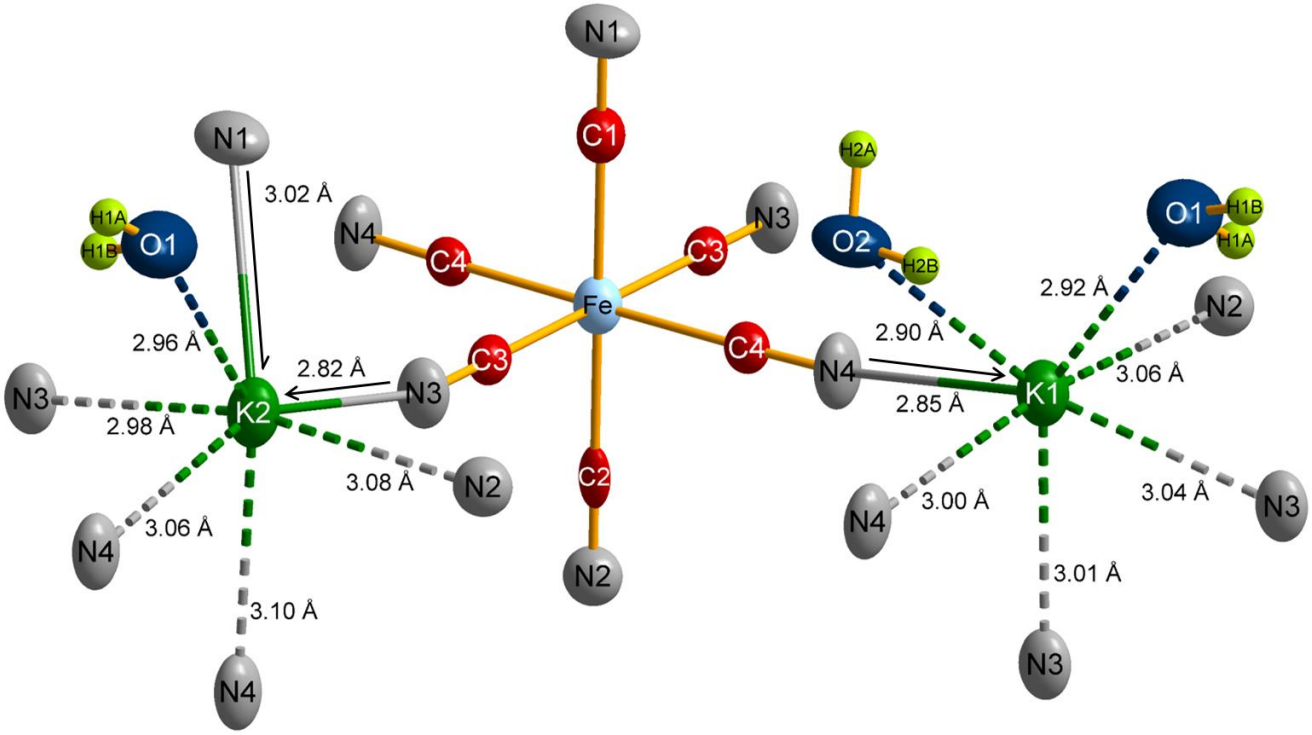


Figure S3. Coordination environment for Fe and K atoms in $K_4[Fe(CN)_6]\cdot 3H_2O$.

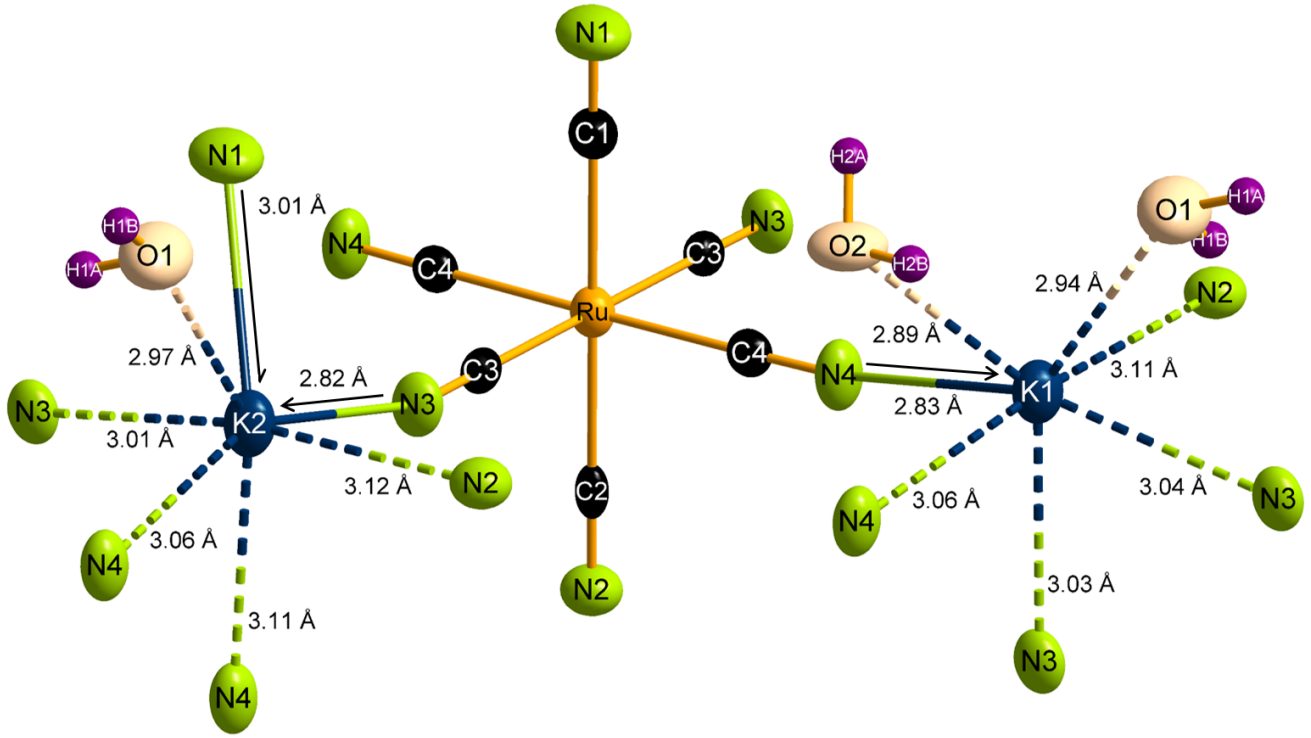


Figure S4. Coordination environment for Ru and K atoms in $K_4[Ru(CN)_6]\cdot 3H_2O$.

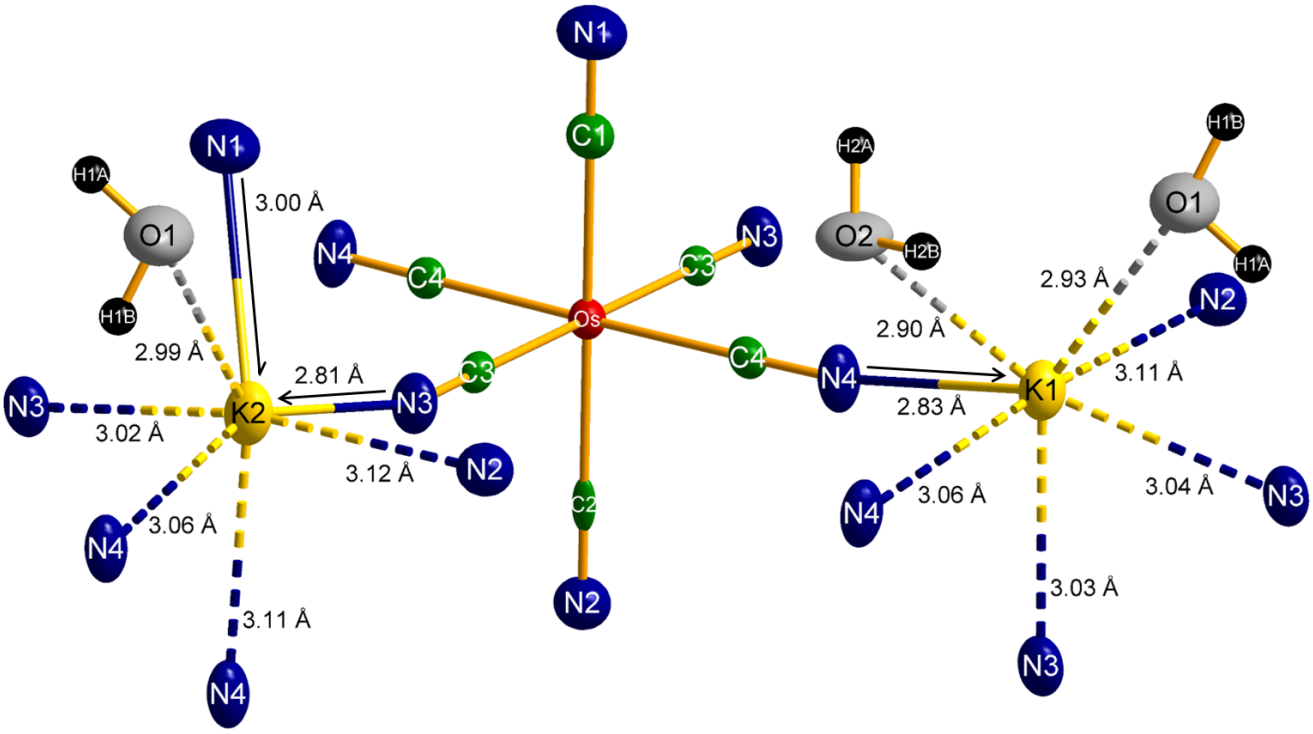


Figure S5. Coordination environment for Os and K atoms in $K_4[Os(CN)_6]\cdot 3H_2O$

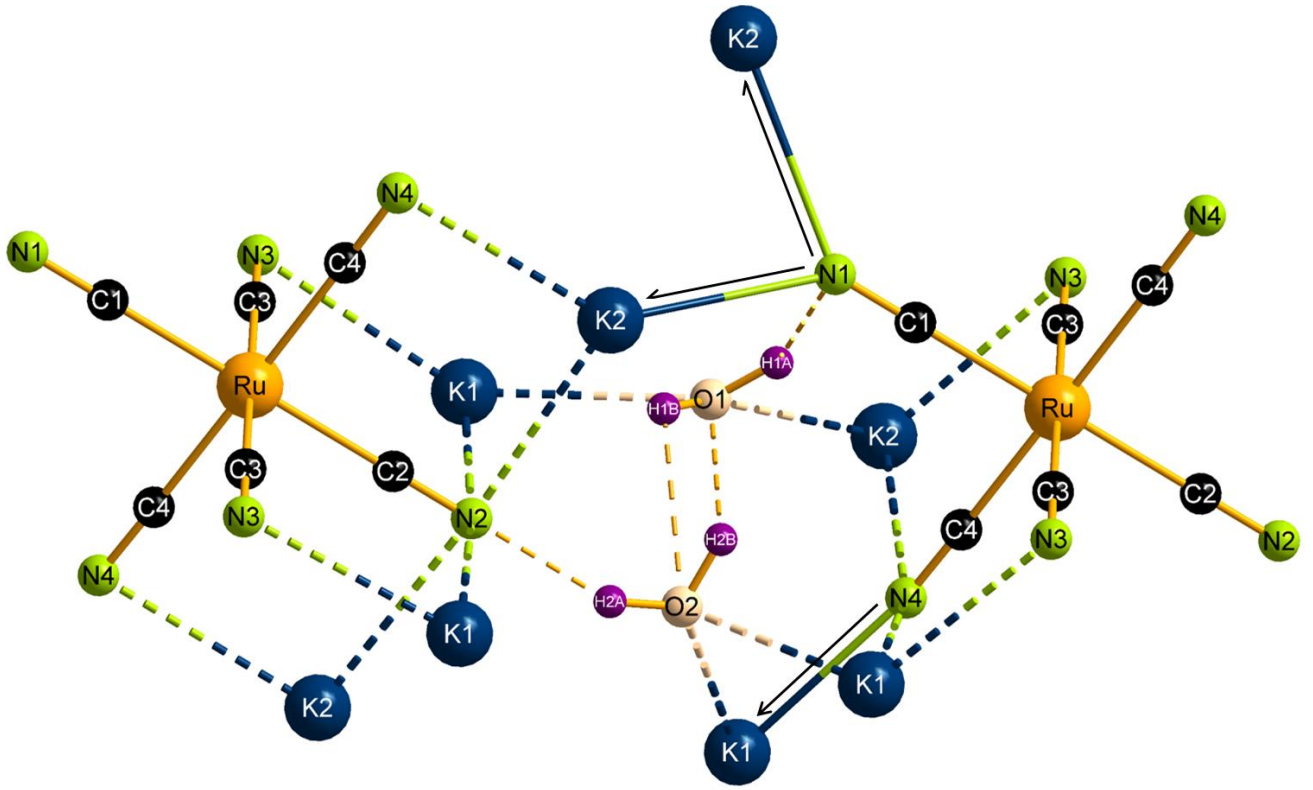


Figure S6. Network of hydrogen bonds and of N-K interactions responsible for large range order in $K_4[Ru(CN)_6]\cdot 3H_2O$.

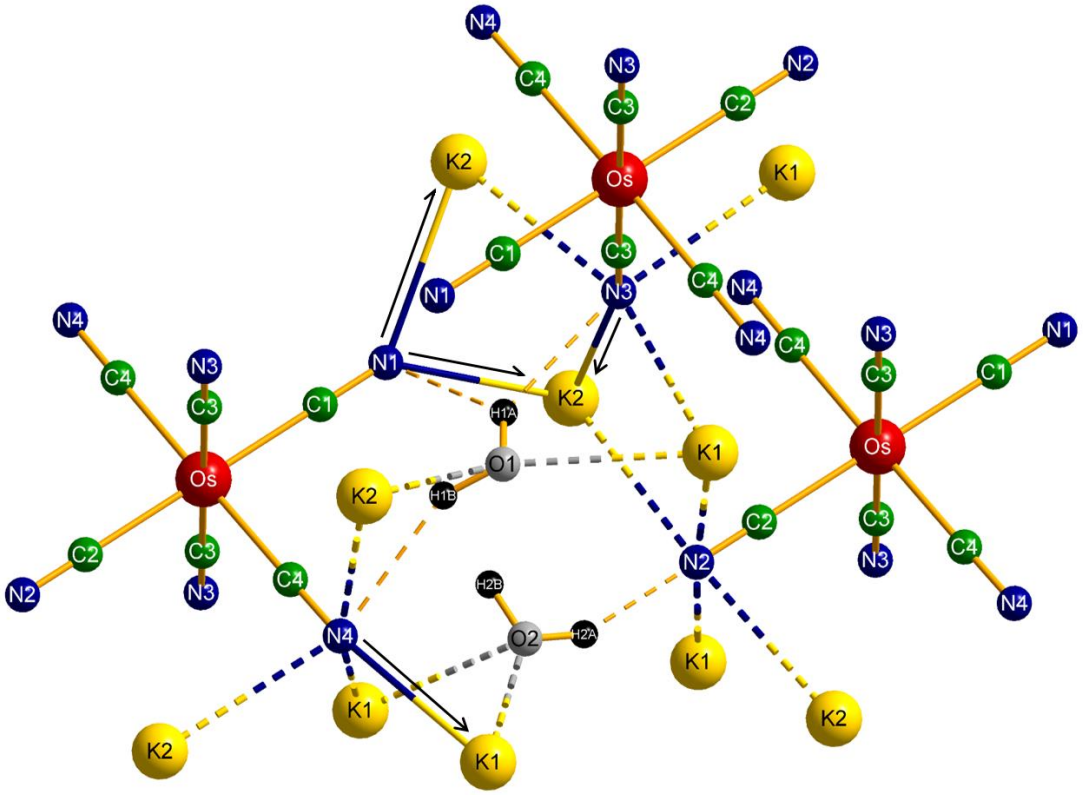


Figure S7. Network of hydrogen bonds and of N-K interactions responsible for large range order in $K_4[Os(CN)_6]\cdot 3H_2O$

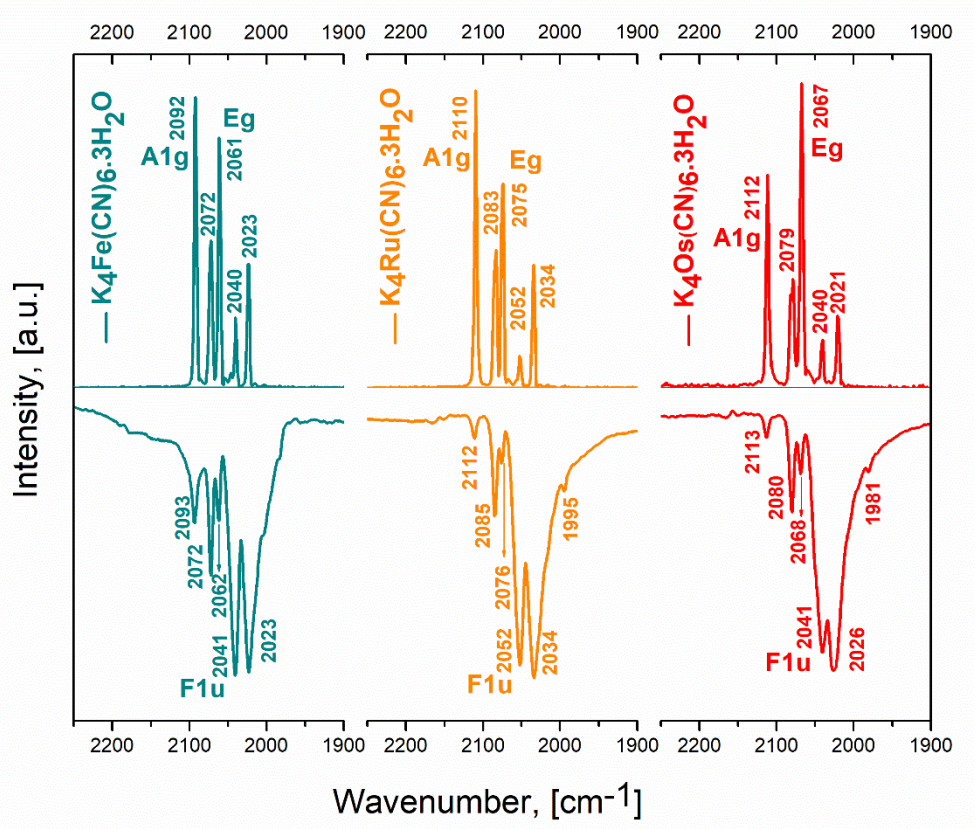


Figure S8. ν(CN) spectral region for the IR (below) and Raman (above) spectra for $K_4[M(CN)_6]$ with M= Fe, Ru, Os

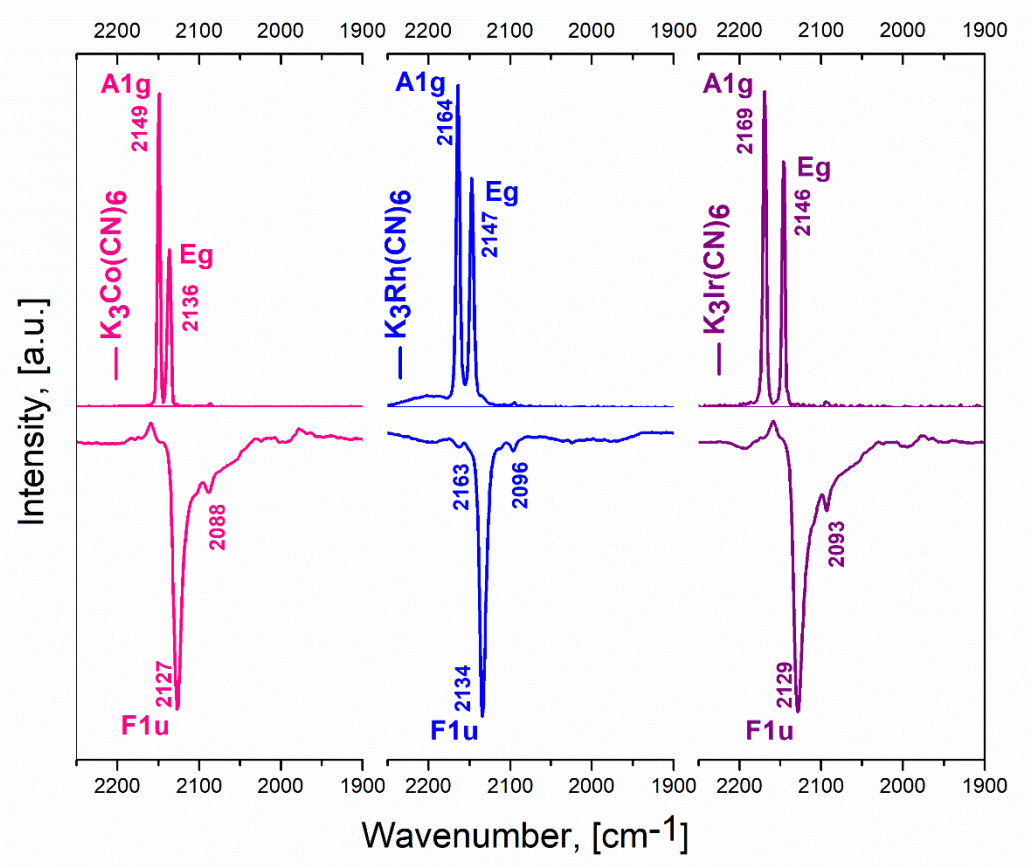


Figure S9. ν(CN) spectral region for the IR (below) and Raman (above) spectra for $K_3[M(CN)_6]$ with M= Co, Rh, Ir

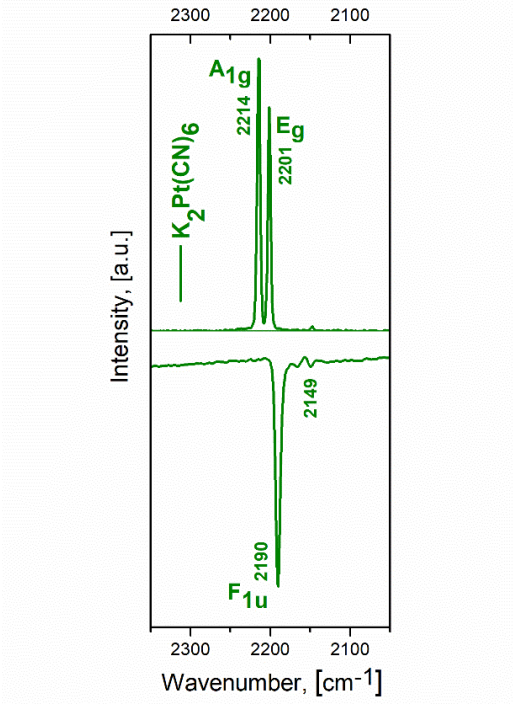


Figure S10. ν(CN) spectral region for the IR (below) and Raman (above) spectra for $K_2[Pt(CN)_6]$

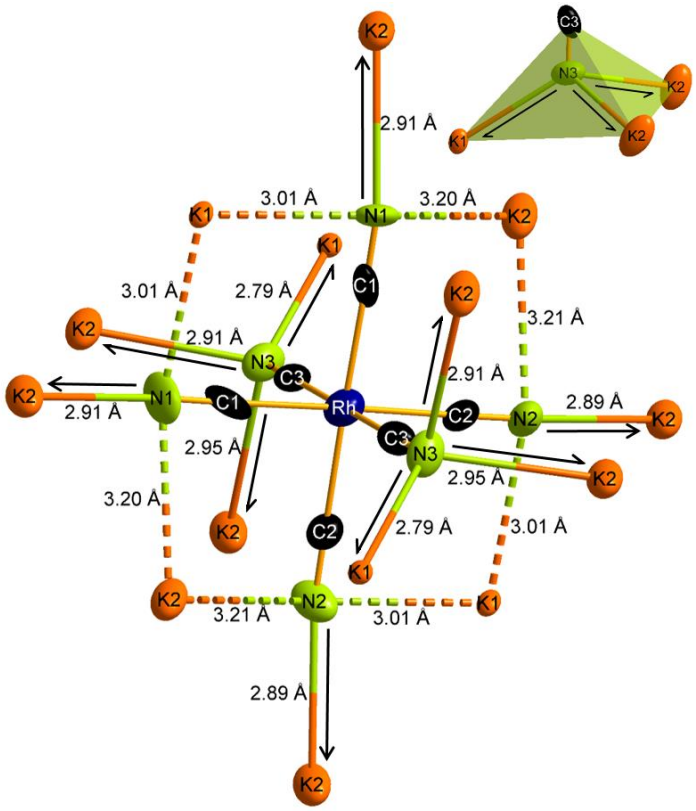


Figure S11. Network of interactions between K atoms and the N end of the CN^- ligands in $K_3[Rh(CN)_6]$

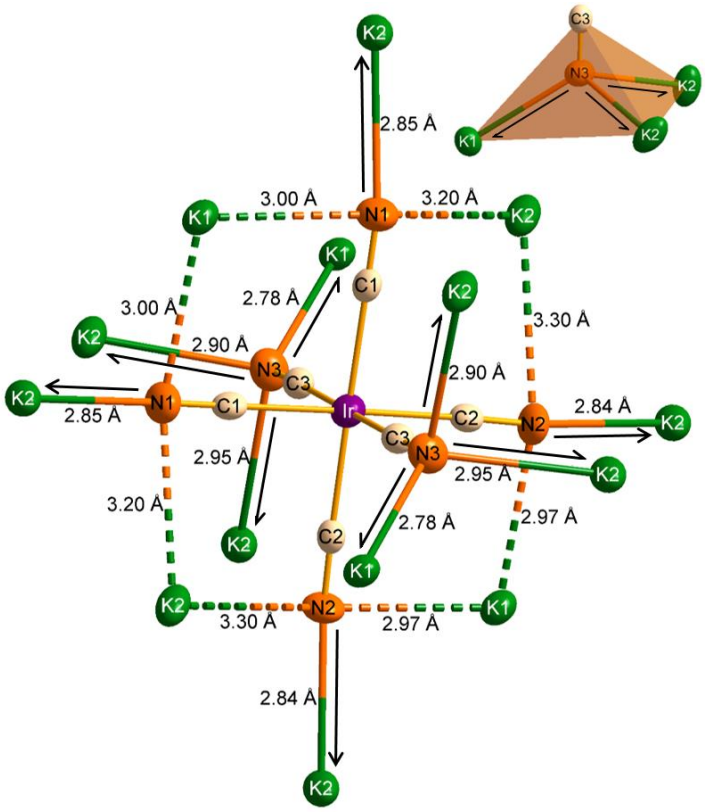


Figure S12. Network of interactions between K atoms and the N end of the CN^- ligands in $K_3[Ir(CN)_6]$

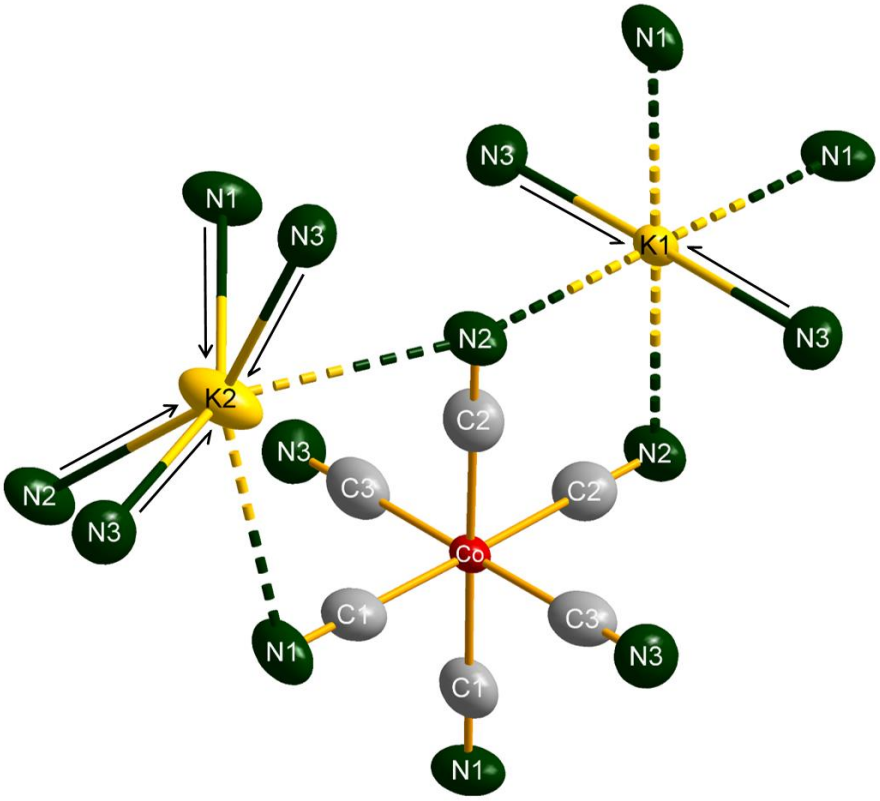


Figure S13. Coordination environment for Co and K atoms in $K_3[Co(CN)_6]$

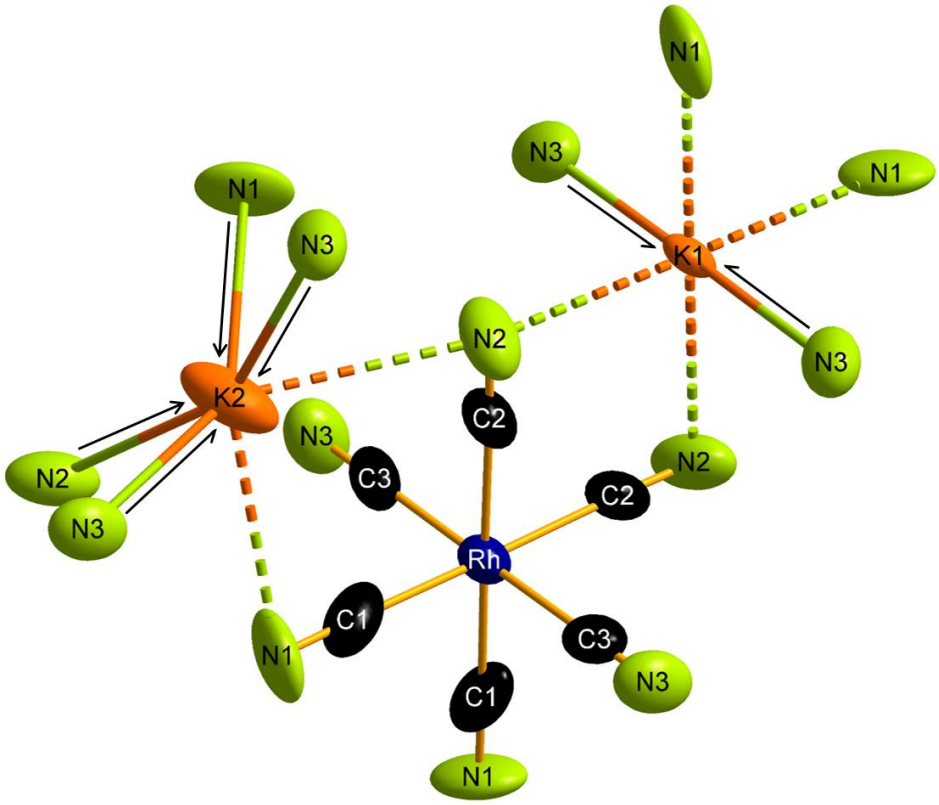


Figure S14. Coordination environment for Rh and K atoms in $K_3[Rh(CN)_6]$

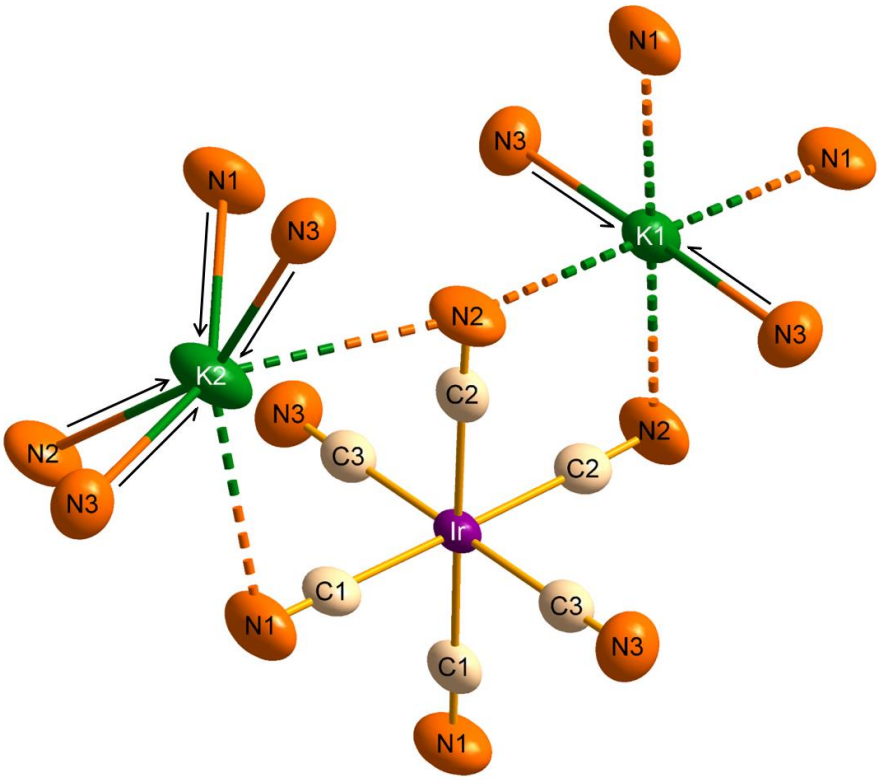


Figure S15. Coordination environment for Ir and K atoms in $K_3[Ir(CN)_6]$

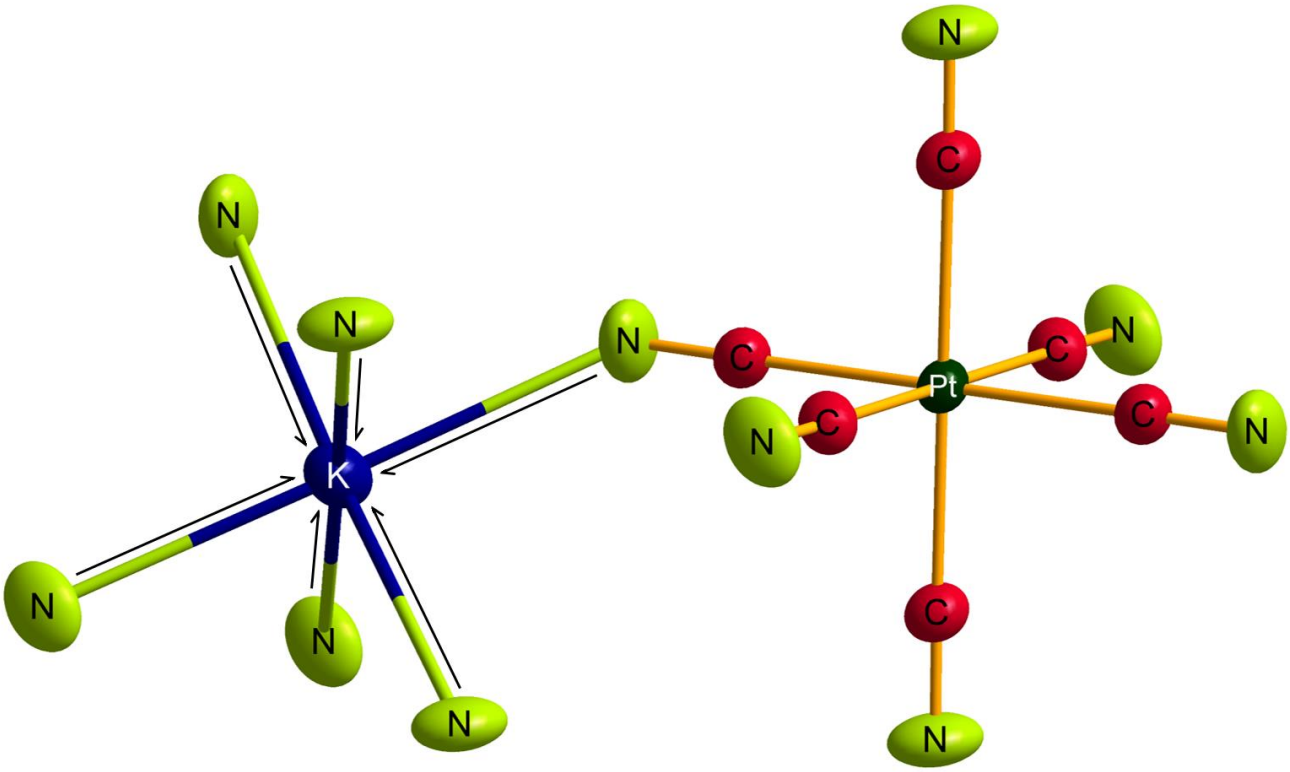


Figure S16. Coordination environment for Pt and K atoms in $K_2[Pt(CN)_6]$.

Table S1. Crystal data and structure refinement for $K_4[M(CN)_6]\cdot 3H_2O$, M=Fe, Ru, Os

Composition	$K_4[Fe(CN)_6]\cdot 3H_2O$	$K_4[Ru(CN)_6]\cdot 3H_2O$	$K_4[Os(CN)_6]\cdot 3H_2O$
Crystal data			
Crystal description	Prism, light yellow	Prism, colorless	Plate, colorless
Crystal size	0.268 x 0.167 x 0.092 mm^3	0.204 x 0.151 x 0.030 mm^3	0.194 x 0.118 x 0.019 mm^3
Empirical formula	$C_6H_6FeK_4N_6O_3$	$C_6H_6K_4N_6O_3Ru$	$C_6H_6K_4N_6O_3Os$
Formula weight	422.42	467.64	556.77
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C 2/c [15]	C 2/c [15]	C 2/c [15]
Unit cell dimensions	a = 9.3940(4) Å	a = 9.4888(3) Å	a = 9.4865(3) Å
	b = 16.8754(8) Å	b = 17.0598(6) Å	b = 17.0659(6) Å
	c = 9.3975(4) Å	c = 9.4998(3) Å	c = 9.4952(3) Å
	β = 90.0100(10)°	β = 90.1760(10)°	β = 90.0900(10)°
Volume	1489.76(11) $Å^3$	1537.79(9) $Å^3$	1537.23(9) $Å^3$
Z	4	4	4
Density (calculated)	1.883 Mg/m^3	2.020 Mg/m^3	2.406 Mg/m^3
Absorption coefficient	2.142 mm^{-1}	2.114 mm^{-1}	9.390 mm^{-1}
F(000)	840	912	1040
Data collection			
Diffractometer	D8 Venture Bruker	D8 Venture Bruker	D8 Venture Bruker
Wavelength	0.71073 Å (Mo kα)	0.71073 Å (Mo kα)	0.71073 Å (Mo kα)
Monochromator	Graphite	Graphite	Graphite
Temperature	296(2) K	296(2) K	296(2) K
Theta range for data collection	3.245 to 26.371°	3.210 to 26.365°	3.210 to 26.372°
Index ranges	-11<=h<=11, -21<=k<=21, -11<=l<=11	-11<=h<=11, -21<=k<=21, -11<=l<=11	-11<=h<=11, -21<=k<=21, -11<=l<=11
Reflections collected	25859	35191	40475
Independent reflections	1097 [R(int) = 0.0418]	1571 [R(int) = 0.0234]	1576 [R(int) = 0.0316]
Completeness to Θ = 25.242°	99.6%	99.7%	99.9%
Refinement			
Absorption correction	Numerical from crystal shape	Numerical from crystal shape	Numerical from crystal shape
Min. and max. transmission	0.598 and 0.827	0.614 and 0.9	0.263 and 0.842
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1097 / 0 / 98	1571 / 0 / 98	1576 / 0 / 98
Goodness-of-fit on F^2	1.115	1.127	1.248
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.1168	R1 = 0.0168, wR2 = 0.0419	R1 = 0.0172, wR2 = 0.0552
R indices (all data)	R1 = 0.0475, wR2 = 0.1226	R1 = 0.0182, wR2 = 0.0425	R1 = 0.0180, wR2 = 0.0555
Largest diff. peak and hole	0.711 and -0.403 $e.Å^{-3}$	0.413 and -0.510 $e.Å^{-3}$	0.936 and -0.888 $e.Å^{-3}$

Table S2. Fractional atomic coordinates, equivalent isotropic displacement parameters and occupation factors for $K_4[M(CN)_6]\cdot 3H_2O$, M=Fe, Ru, Os

Structure	Site	x	y	z	U_{eq} (Å^2)	Occ
$K_4[Fe(CN)_6]\cdot 3H_2O$						
K1	8f	0.5968(1)	0.1440(1)	0.4389(1)	0.033(1)	1
K2	8f	0.3141(1)	0.3585(1)	0.3436(1)	0.034(1)	1
Fe	4e	0	0.1773(1)	1/4	0.017(1)	1
C1	4e	0	0.0637(3)	1/4	0.029(1)	1
N1	4e	0	-0.0055(3)	1/4	0.044(1)	1
C2	4e	0	0.2920(3)	1/4	0.020(1)	1
N2	4e	0	0.3580(3)	1/4	0.032(1)	1
C3	8f	0.0680(4)	0.1775(2)	0.0576(4)	0.022(1)	1
N3	8f	0.1093(4)	0.1775(2)	-0.0603(4)	0.034(1)	1
C4	8f	0.1927(4)	0.1769(2)	0.3187(4)	0.022(1)	1
N4	8f	0.3086(4)	0.1752(2)	0.3612(4)	0.036(1)	1
O1	8f	0.2430(5)	-0.0021(2)	0.4849(7)	0.083(2)	1
H1A	8f	0.2619	-0.0338	0.4023	0.124	1
H1B	8f	0.1488	0.0185	0.4699	0.124	1
O2	8f	0.4661(10)	0.0282(3)	0.2803(11)	0.056(3)	0.50(1)
H2A	4e	1/2	-0.0228	1/4	0.084	1
H2B	8f	0.3669	0.0285	0.2555	0.084	0.50(1)
$K_4[Ru(CN)_6]\cdot 3H_2O$						
K1	8f	0.5998(1)	0.1440(1)	0.4390(1)	0.032(1)	1
K2	8f	0.3146(1)	0.3579(1)	0.3463(1)	0.033(1)	1
Ru	4e	0	0.1778(1)	1/4	0.015(1)	1
C1	4e	0	0.0582(2)	1/4	0.027(1)	1
N1	4e	0	-0.0093(2)	1/4	0.051(1)	1
C2	4e	0	0.2982(2)	1/4	0.019(1)	1
N2	4e	0	0.3641(1)	1/4	0.034(1)	1
C3	8f	0.0723(2)	0.1780(1)	0.0480(2)	00.20(1)	1
N3	8f	0.1129(2)	0.1785(1)	-0.0666(2)	0.031(1)	1
C4	8f	0.2018(2)	0.1773(1)	0.3236(2)	0.020(1)	1
N4	8f	0.3159(2)	0.1761(1)	0.3659(2)	0.034(1)	1
O1	8f	0.2408(3)	-0.0020(1)	0.4867(3)	0.087(1)	1
H1A	8f	0.1543	0.0187	0.4496	0.130	1
H1B	8f	0.2740	-0.0372	0.4153	0.130	1
O2	8f	0.4617(4)	0.0303(2)	0.2778(5)	0.059(1)	0.50(1)
H2A	4e	1/2	-0.0195	1/4	0.088	1
H2B	8f	0.3621	0.0256	0.2615	0.088	0.50(1)
$K_4[Os(CN)_6]\cdot 3H_2O$						
K1	8f	0.5999(1)	0.1439(1)	0.4389(1)	0.028(1)	1
K2	8f	0.3149(1)	0.3580(1)	0.3463(1)	0.028(1)	1
Os	4e	0	0.1780(1)	1/4	0.015(1)	1
C1	4e	0	0.0581(3)	1/4	0.023(1)	1
N1	4e	0	-0.0094(4)	1/4	0.045(2)	1
C2	4e	0	0.2995(3)	1/4	0.014(1)	1
N2	4e	0	0.3640(3)	1/4	0.029(1)	1
C3	8f	0.0723(4)	0.1781(2)	0.0475(4)	0.014(1)	1
N3	8f	0.1136(4)	0.1787(2)	-0.0669(4)	0.026(1)	1
C4	8f	0.2021(4)	0.1773(2)	0.3241(4)	0.015(1)	1
N4	8f	0.3165(4)	0.1762(2)	0.3663(4)	0.028(1)	1
O1	8f	0.2416(6)	-0.0026(3)	0.4857(6)	0.077(2)	1
H1A	8f	0.1739	-0.0361	0.4407	0.116	1
H1B	8f	0.2291	0.0474	0.4408	0.116	1
O2	8f	0.4609(9)	0.0293(4)	0.2777(11)	0.055(2)	0.50(1)
H2A	4e	1/2	-0.0203	1/4	0.083	1
H2B	8f	0.3622	0.0247	0.2567	0.083	0.50(1)

Table S3. Selected bond distances and bond angles for $K_4[M(CN)_6]\cdot 3H_2O$, M=Fe, Ru, Os

Structure	Atoms	Bond distance (Å)	Atoms	Bond angle (°)
$K_4[Fe(CN)_6]\cdot 3H_2O$	Fe-C1	1.917(5)	N1-C1-Fe	180.0
	Fe-C2	1.936(5)	N2-C2-Fe	180.0
	Fe-C3	1.918(4)	N3-C3-Fe	179.8(4)
	Fe-C4	1.922(4)	N4-C4-Fe	178.7(3)
	C1-N1	1.168(7)	C1-N1-K2	139.57(6)
	C2-N2	1.113(8)	C2-N2-K1	89.37(9)
	C3-N3	1.174(6)	C2-N2-K2	90.16(9)
	C4-N4	1.159(5)	C3-N3-K1	86.9(2)
	K1-N2	3.0616(10)	C3-N3-K2	88.8(3)
	K1-N3	3.014(4)	C3-N3-K1	89.4(3)
	K1-N3	3.041(4)	C3-N3-K2	166.9(3)
	K1-N4	2.853(3)	C4-N4-K1	87.7(3)
	K1-N4	3.004(4)	C4-N4-K2	87.9(3)
	K1-O1	2.918(4)	C4-N4-K2	88.5(3)
	K1-O2	2.748(9)	C4-N4-K1	169.5(3)
	K1-O2	2.901(9)		
	K2-N1	3.016(4)		
	K2-N2	3.0784(9)		
	K2-N3	2.825(4)		
	K2-N3	2.979(4)		
	K2-N4	3.057(5)		
	K2-N4	3.097(4)		
	K2-O1	2.959(5)		
$K_4[Ru(CN)_6]\cdot 3H_2O$	Ru-C1	2.040(3)	N1-C1-Ru	180.0
	Ru-C2	2.054(3)	N2-C2-Ru	180.0
	Ru-C3	2.0396(17)	N3-C3-Ru	179.62(17)
	Ru-C4	2.0364(17)	N4-C4-Ru	179.19(16)
	C1-N1	1.151(4)	C1-N1-K2	138.78(3)
	C2-N2	1.126(4)	C2-N2-K1	87.45(4)
	C3-N3	1.156(2)	C2-N2-K2	88.04(4)
	C4-N4	1.154(2)	C3-N3-K1	85.66(12)
	K1-N2	3.1079(4)	C3-N3-K2	86.64(12)
	K1-N3	3.0316(18)	C3-N3-K1	88.70(12)
	K1-N3	3.0379(17)	C3-N3-K2	165.93(15)
	K1-N4	2.8337(17)	C4-N4-K1	85.49(12)
	K1-N4	3.0573(18)	C4-N4-K2	86.13(12)
	K1-O1	2.940(2)	C4-N4-K2	87.61(12)
	K1-O2	2.795(4)	C4-N4-K1	168.26(15)
	K1-O2	2.888(4)		
	K2-N1	3.013(2)		
	K2-N2	3.1209(4)		
	K2-N3	2.8160(16)		
	K2-N3	3.0115(18)		
	K2-N4	3.0605(18)		
	K2-N4	3.1065(19)		
	K2-O1	2.974(2)		

Table S3. Continued

Structure	Atoms	Bond distance (Å)	Atoms	Bond angle (°)
	Os-C1	2.046(6)	N1-C1-Os	180.0
	Os-C2	2.073(6)	N2-C2-Os	180.0
	Os-C3	2.043(4)	N3-C3-Os	179.5(3)
	Os-C4	2.041(4)	N4-C4-Os	179.4(3)
	C1-N1	1.152(9)	C1-N1-K2	138.80(8)
	C2-N2	1.101(8)	C2-N2-K1	87.53(11)
	C3-N3	1.155(6)	C2-N2-K2	88.13(11)
	C4-N4	1.157(6)	C3-N3-K1	85.8(3)
	K1-N2	3.1067(9)	C3-N3-K2	86.3(3)
	K1-N3	3.032(4)	C3-N3-K1	88.7(2)
	K1-N3	3.035(4)	C3-N3-K2	165.6(3)
$K_4[Os(CN)_6]\cdot 3H_2O$	K1-N4	2.828(4)	C4-N4-K1	85.4(3)
	K1-N4	3.056(4)	C4-N4-K2	85.9(3)
	K1-O1	2.930(5)	C4-N4-K2	87.6(3)
	K1-O2	2.810(9)	C4-N4-K1	168.2(3)
	K1-O2	2.895(9)		
	K2-N1	3.008(5)		
	K2-N2	3.1239(9)		
	K2-N3	2.809(4)		
	K2-N3	3.016(4)		
	K2-N4	3.059(4)		
	K2-N4	3.109(4)		
	K2-O1	2.987(5)		

Table S4. Crystal data and structure refinement for $K_3[M(CN)_6]$, M=Co, Rh, Ir

Composition	$K_3[Co(CN)_6]$	$K_3[Rh(CN)_6]$	$K_3[Ir(CN)_6]$
Crystal data			
Crystal description	Plate, colorless	Plate, colorless	Plate, colorless
Crystal size	0.204 x 0.151 x 0.030 mm^3	0.181 x 0.177 x 0.026 mm^3	0.151 x 0.114 x 0.021 mm^3
Empirical formula	$C_6CoK_3N_6$	$C_6K_3N_6Rh$	$C_6IrK_3N_6$
Formula weight	332.35	376.33	465.62
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P b c n [60]	P b c n [60]	P b c n [60]
Unit cell dimensions	a = 10.3511(5) Å	a = 10.5092(16) Å	a = 10.5320(4) Å
	b = 8.3612(4) Å	b = 8.4568(12) Å	b = 8.4511(3) Å
	c = 13.3549(7) Å	c = 13.5808(19) Å	c = 13.5945(5) Å
Volume	1155.84(10) $Å^3$	1207.0(3) $Å^3$	1210.01(8) $Å^3$
Z	4	4	4
Density (calculated)	1.910 Mg/m^3	2.071 Mg/m^3	2.556 Mg/m^3
Absorption coefficient	2.542 mm^{-1}	2.428 mm^{-1}	12.045 mm^{-1}
F(000)	648	720	848
Data collection			
Diffractometer	D8 Venture Bruker	D8 Venture Bruker	D8 Venture Bruker
Wavelength	0.71073 Å (Mo kα)	0.71073 Å (Mo kα)	0.71073 Å (Mo kα)
Monochromator	Graphite	Graphite	Graphite
Temperature	296(2) K	296(2) K	296(2) K
Theta range for data collection	3.484 to 26.372°	3.572 to 26.371°	3.567 to 26.364°
Index ranges	-12<=h<=12, -10<=k<=10, -16<=l<=16	-13<=h<=13, -10<=k<=10, -16<=l<=16	-12<=h<=13, -10<=k<=10, -16<=l<=16
Reflections collected	60218	12201	30455
Independent reflections	1183 [R(int) = 0.0374]	632 [R(int) = 0.0679]	1232 [R(int) = 0.0347]
Completeness to Θ = 25.242°	99.5%	99.6%	99.5%
Refinement			
Absorption correction	Numerical from crystal shape	Numerical from crystal shape	Numerical from crystal shape
Min. and max. transmission	0.625 and 0.928	0.668 and 0.94	0.264 and 0.286
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1184 / 0 / 74	632 / 0 / 74	1232 / 0 / 74
Goodness-of-fit on F^2	1.142	1.069	1.208
Final R indices [I>2sigma(I)]	R1 = 0.0687, wR2 = 0.1235	R1 = 0.0573, wR2 = 0.1189	R1 = 0.0170, wR2 = 0.0385
R indices (all data)	R1 = 0.0899, wR2 = 0.1452	R1 = 0.0853, wR2 = 0.1363	R1 = 0.0285, wR2 = 0.0427
Largest diff. peak and hole	0.792 and -0.481 $e.Å^{-3}$	0.787 and -0.578 $e.Å^{-3}$	0.371 and -0.866 $e.Å^{-3}$

Table S5. Fractional atomic coordinates, equivalent isotropic displacement parameters and occupation factors for $K_3[M(CN)_6]$, M=Co, Rh, Ir

Structure	Site	x	y	z	U_{eq} (Å^2)	Occ
$K_3[Co(CN)_6]$						
K1	4c	0	0.6265(1)	1/4	0.016(1)	1
K2	8d	0.2681(2)	0.1240(1)	-0.0011(1)	0.035(1)	1
Co	4c	0	0.1239(1)	1/4	0.013(1)	1
C1	8d	0.0531(4)	-0.0342(5)	0.1590(3)	0.027(1)	1
N1	8d	0.0857(5)	-0.1317(4)	0.1024(3)	0.031(1)	1
C2	8d	0.0502(4)	0.2838(5)	0.1576(3)	0.025(1)	1
N2	8d	0.0816(4)	0.3811(4)	0.1031(3)	0.029(1)	1
C3	8d	0.1663(5)	0.1247(5)	0.3102(3)	0.027(1)	1
N3	8d	0.2619(4)	0.1241(4)	0.3490(4)	0.029(1)	1
$K_3[Rh(CN)_6]$						
K1	4c	0	0.6267(5)	1/4	0.016(1)	1
K2	8d	0.2639(4)	0.1242(5)	-0.0017(2)	0.047(1)	1
Rh	4c	0	0.1238(2)	1/4	0.022(1)	1
C1	8d	0.0549(12)	-0.0400(18)	0.1533(10)	0.032(3)	1
N1	8d	0.0859(11)	-0.1359(16)	0.0990(8)	0.043(3)	1
C2	8d	0.0550(12)	0.2935(13)	0.1543(9)	0.028(3)	1
N2	8d	0.0887(11)	0.3874(15)	0.1014(8)	0.040(3)	1
C3	8d	0.1746(10)	0.1248(16)	0.3142(8)	0.030(2)	1
N3	8d	0.2677(9)	0.1246(18)	0.3500(7)	0.035(2)	1
$K_3[Ir(CN)_6]$						
K1	4c	0	0.6283(2)	1/4	0.027(1)	1
K2	8d	0.2693(1)	0.1231(1)	-0.0019(1)	0.039(1)	1
Ir	4c	0	0.1240(1)	1/4	0.017(1)	1
C1	8d	0.0565(4)	-0.0435(4)	0.1526(3)	0.025(1)	1
N1	8d	0.0885(3)	-0.1384(4)	0.0982(3)	0.041(1)	1
C2	8d	0.0554(4)	0.2939(4)	0.1542(3)	0.023(1)	1
N2	8d	0.0857(4)	0.3932(4)	0.1014(3)	0.038(1)	1
C3	8d	0.1737(3)	0.1238(5)	0.3130(2)	0.024(1)	1
N3	8d	0.2707(3)	0.1255(6)	0.3510(2)	0.034(1)	1

Table S6. Selected bond distances and bond angles for $K_3[M(CN)_6]$, M=Co, Rh, Ir.

Structure	Atoms	Bond distance (Å)	Atoms	Bond angle (°)
$K_3[Co(CN)_6]$	Co-C1	1.878(4)	N1-C1-Co	179.7(4)
	Co-C2	1.892(4)	N2-C2-Co	178.9(4)
	Co-C3	1.902(5)	N3-C3-Co	177.3(5)
	C1-N1	1.162(5)	C1-N1-K1	87.6(3)
	C2-N2	1.140(6)	C1-N1-K2	89.1(3)
	C3-N3	1.115(7)	C1-N1-K2	163.4(4)
	K1-N1	2.960(4)	C2-N2-K2	88.3(3)
	K1-N2	2.962(4)	C2-N2-K1	89.4(3)
	K1-N3	2.797(5)	C2-N2-K2	162.9(4)
	K2-N1	2.894(4)	C3-N3-K2	102.8(4)
	K2-N1	3.170(4)	C3-N3-K2	110.2(4)
	K2-N2	2.912(4)	C3-N3-K1	124.1(4)
	K2-N2	3.206(4)		
	K2-N3	2.883(4)		
	K2-N3	2.922(5)		
$K_3[Rh(CN)_6]$	Rh-C1	1.994(15)	N1-C1-Rh	178.8(12)
	Rh-C2	2.020(12)	N2-C2-Rh	178.3(11)
	Rh-C3	2.032(12)	N3-C3-Rh	178.9(11)
	C1-N1	1.143(18)	C1-N1-K1	87.0(9)
	C2-N2	1.128(16)	C1-N1-K2	87.4(10)
	C3-N3	1.093(14)	C1-N1-K2	162.1(11)
	K1-N1	3.009(13)	C2-N2-K1	87.0(8)
	K1-N2	3.006(11)	C2-N2-K2	88.3(9)
	K1-N3	2.794(10)	C2-N2-K2	164.5(10)
	K2-N1	2.912(12)	C3-N3-K2	101.7(10)
	K2-N1	3.195(14)	C3-N3-K2	107.2(11)
	K2-N2	2.893(13)	C3-N3-K1	124.5(9)
	K2-N2	3.210(12)		
	K2-N3	2.913(14)		
	K2-N3	2.945(13)		
$K_3[Ir(CN)_6]$	Ir-C1	2.027(4)	N1-C1-Ir	179.6(4)
	Ir-C2	2.025(4)	N2-C2-Ir	178.3(3)
	Ir-C3	2.019(4)	N3-C3-Ir	178.1(3)
	C1-N1	1.142(5)	C1-N1-K1	85.7(3)
	C2-N2	1.149(5)	C1-N1-K2	88.1(3)
	C3-N3	1.145(4)	C1-N1-K2	163.6(3)
	K1-N1	3.003(4)	C2-N2-K2	85.6(3)
	K1-N2	2.973(4)	C2-N2-K1	88.8(3)
	K1-N3	2.778(3)	C2-N2-K2	163.1(3)
	K2-N1	2.856(4)	C3-N3-K2	100.8(3)
	K2-N1	3.218(4)	C3-N3-K2	107.3(3)
	K2-N2	2.843(3)	C3-N3-K1	123.6(3)
	K2-N2	3.304(4)		
	K2-N3	2.901(4)		
	K2-N3	2.949(4)		

Table S7. Crystal data and structure refinement for $K_2[Pt(CN)_6]$

Composition	$K_2[Pt(CN)_6]$
Crystal data	
Crystal description	Prism, colorless
Crystal size	0.275 x 0.210 x 0.054 mm^3
Empirical formula	$C_6K_2N_6Pt$
Formula weight	429.41
Crystal system	Trigonal
Space group	P -3 1 m [162]
Unit cell dimensions	a = 7.3928(4) Å
	c = 6.6613(3) Å
Volume	315.29(4) $Å^3$
Z	1
Density (calculated)	2.262 Mg/m^3
Absorption coefficient	11.763 mm^{-1}
F(000)	194
Data collection	
Diffractometer	D8 Venture Bruker
Wavelength	0.71073 Å (Mo kα)
Monochromator	Graphite
Temperature	296(2) K
Theta range for data collection	6.374 to 26.362°
Index ranges	-9<=h<=9, -9<=k<=9,
	-8<=l<=8
Reflections collected	7539
Independent reflections	242 [R(int) = 0.0304]
Completeness to Θ = 25.242°	95%
Refinement	
Absorption correction	Numerical from crystal shape
Min. and max. transmission	0.14 and 0.569
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	242 / 0 / 17
Goodness-of-fit on F^2	1.210
Final R indices [I>2sigma(I)]	R1 = 0.0119, wR2 = 0.0281
R indices (all data)	R1 = 0.0119, wR2 = 0.0281
Largest diff. peak and hole	0.443 and -0.617 e.$Å^{-3}$

Table S8. Fractional atomic coordinates, equivalent isotropic displacement parameters and occupation factors for $K_2[Pt(CN)_6]$

Structure	Site	x	y	z	U_{eq} (Å^2)	Occ
$K_2[Pt(CN)_6]$						
K	2d	1/3	2/3	1/2	0.036(1)	1
Pt	1a	0	0	0	0.019(1)	1
C	6k	0.2222(5)	0.2222(5)	0.1748(5)	0.031(1)	1
N	6k	0.3460(5)	0.3460(5)	0.2753(5)	0.050(1)	1

Table S9. Selected bond distances and bond angles for $K_2[Pt(CN)_6]$.

Structure	Atoms	Bond distance (Å)	Atoms	Bond angle (°)
$K_2[Pt(CN)_6]$	Pt-C	2.014(4)	N-C-Pt	179.1(4)
	C-N	1.134(5)	C-N-K	129.32(10)
	K-N	2.845(2)		

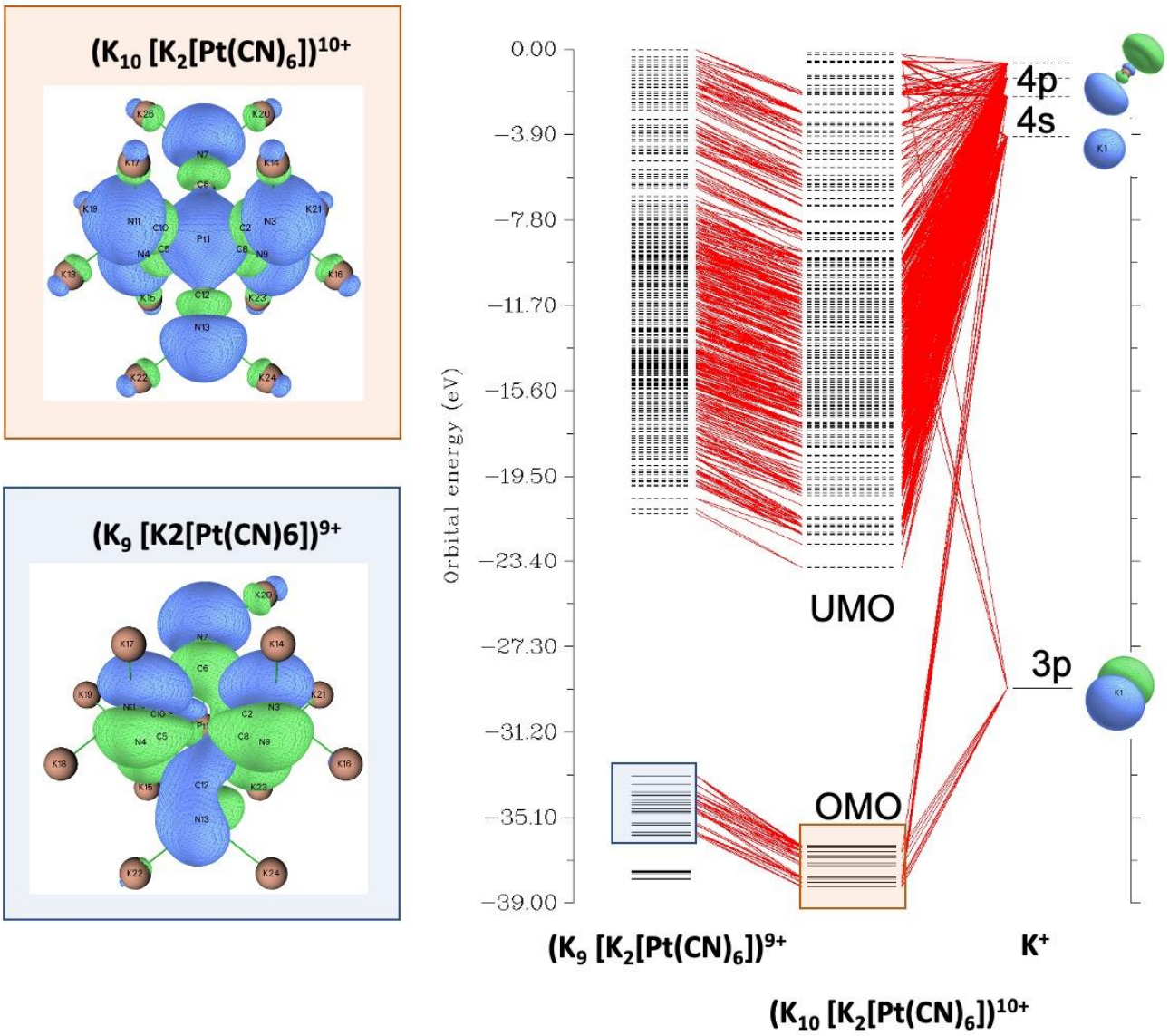


Figure S17. Orbital interaction diagram determined by CDA analysis for fragment A ($(K_9[K_2[Pt(CN)_6])^{9+}$) and fragment B (K^+) to form the complex ($(K_{10}[K_2[Pt(CN)_6])^{10+}$). Occupied (OMO) and unoccupied (UMO) molecular orbitals are represented as solid and dashed lines, respectively. The red lines represent the contribution of the molecular orbitals of the fragments to the complex. Representative orbitals of the interaction and the complex are included.

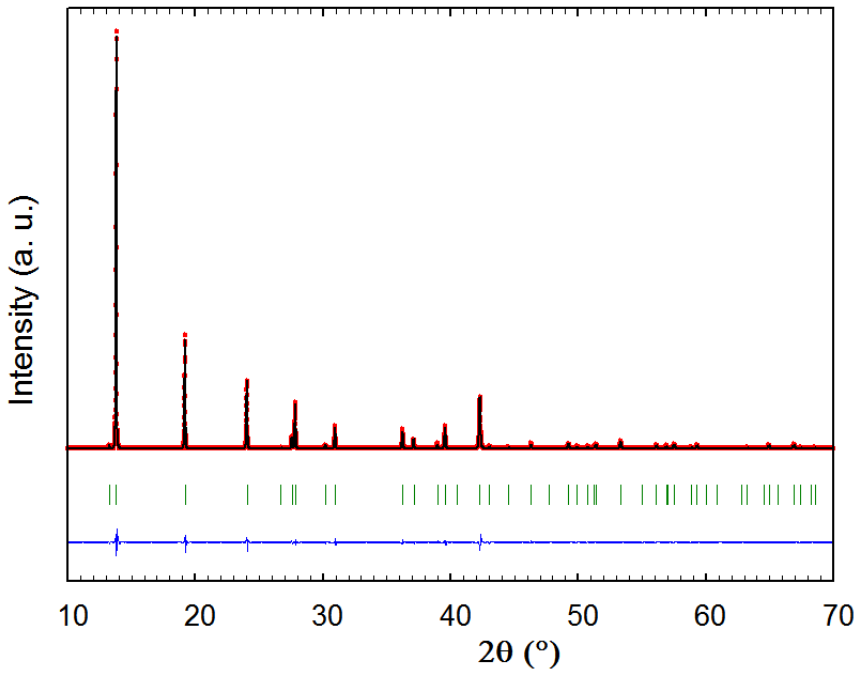


Figure S18. XRD powder pattern observed (red), calculated (black) and difference profiles (blue) for the Le Bail refinement of $K_2[Pt(CN)_6]$ complex. The crystalline phase was identified according to ICSD file number 43076. Similar XRD powder patterns, corresponding to a single phase of the sample under study, were obtained for the remaining K salts.

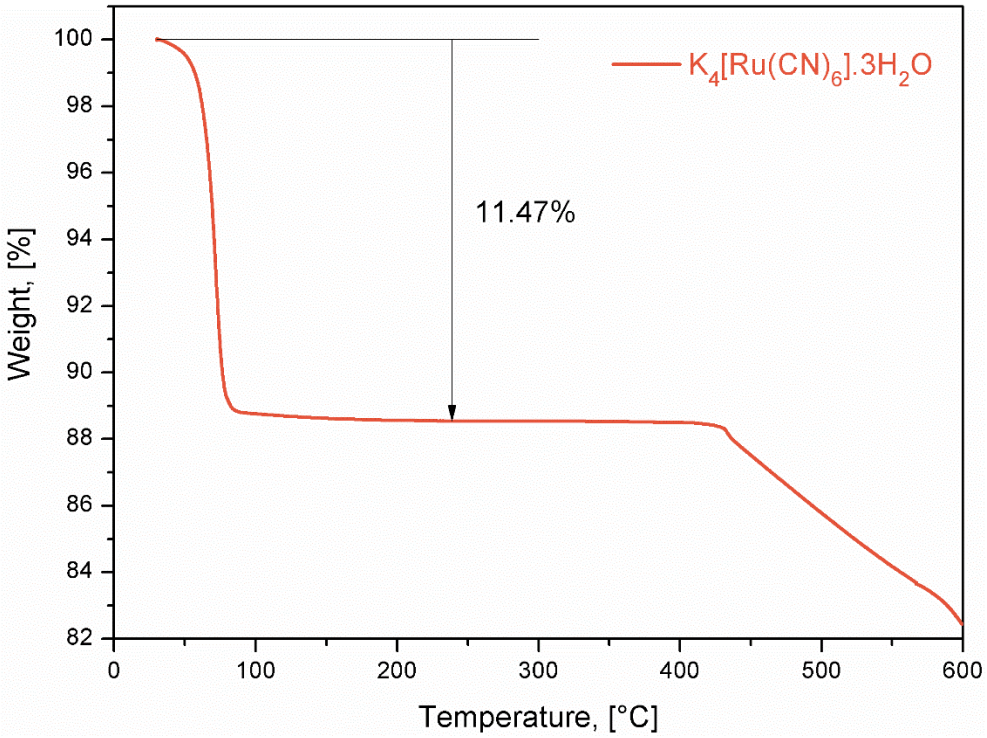
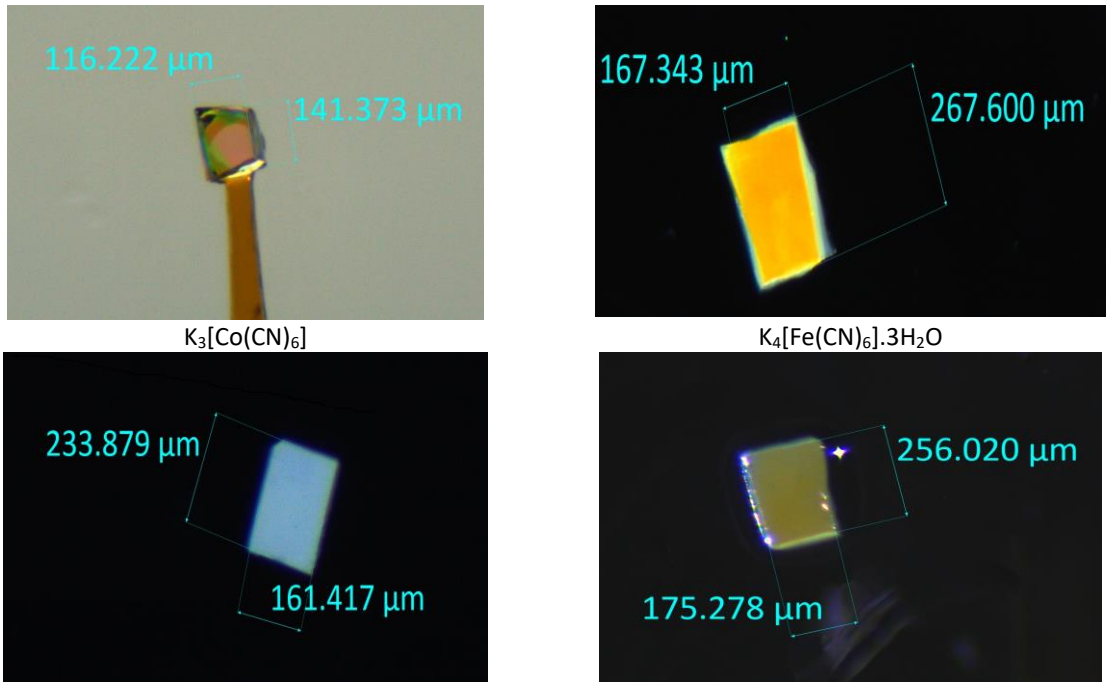


Figure S19. TG curve for the crystals of $K_4[Ru(CN)_6].xH_2O$. For all the samples under study TG data were recorded to obtain the number of water molecules per formula unit.



$K_3[Co(CN)_6]$ $K_4[Fe(CN)_6].3H_2O$

$K_4[Os(CN)_6].3H_2O$ $K_4[Ru(CN)_6].3H_2O$

Figure S20. Typical single crystal size used for the structural study.