Supporting Information

Characterization of a mixed-valence Ru(II)/Ru(III) ion-pair complex. Unexpected HF-EPR evidence for Ru(III)-Ru(III) dimer coupling

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Contents

X-ray structure of $[Ru^{II}(bipy)_2(pic)]Cl\cdot 5.5H_2O$

The orange plate crystals of $[Ru^{II}(bipy)_2(pic)]Cl\cdot 5.5H_2O$ were obtained from an aqueous solution. The X-ray structure reported in Ref. 21 was for the complex $[Ru^{II}(bipy)_2(pic)]Cl\cdot CH_3CN\cdot 1.5H_2O$ that was obtained from an acetonitrile solution of $[Ru^{II}(bipy)_2(pic)]Cl$. In the present case it was necessary to know the number of water molecules contained in the crystal. The X-ray data were recorded and processed in the same way as described in the main text. The data collection and refinement processes are summarized in Table S1. The structural data have been deposited at the Cambridge Crystallographic Data Centre: CCDC No 1909847.

Table S1. Crystal data and structure refinement parameters for $[Ru^{II}(bipy)_2(pic)]Cl\cdot 5.5H_2O$.

Identification code	$[Ru^{II}(bipy)_2(pic)]Cl\cdot 5.5H_2O$
CCDC	1909847
Empirical formula	$C_{26}H_{31}Cl_1Ru_1N_5O_{7.5}$
Formula weight. g mol^{-1}	670.08
Crystal size. mm	0.417 x 0.089 x 0.069
Crystal system	Monoclinic
Space group	$P2_1/n$
a. Å	19.7450(15)
b. Å	13.5904(8)
c. Å	22.8195(17)
β. deg	100.691(8)
Volume. $Å^3$	6017.1(7)
Z	8
Density (calc.). g cm^{-3}	1.479
Absorption coefficient. mm^{-1}	0.662
F(000)	2744
Θ range. deg	2.355 to 28.366
Reflections collected / unique	43554 / 13639 [R(int) = 0.1822]
Index ranges *hkl*	-25<=h<=26, -16<=k<=17, -29<=l<=30
restraints/parameters	6 / 730

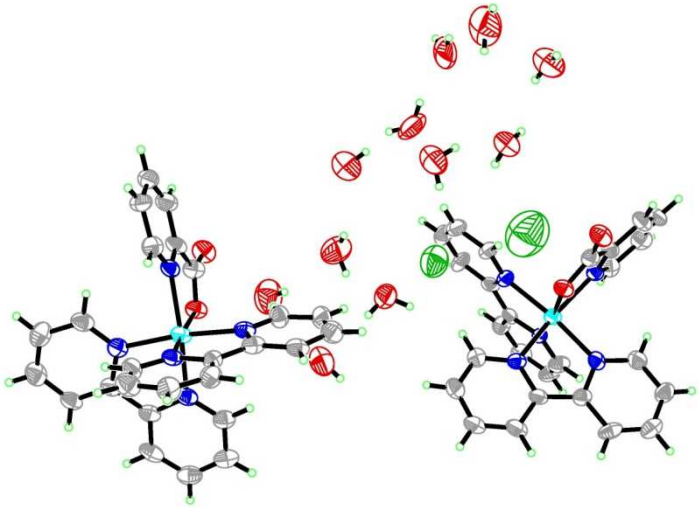
Goodness of fit on F^2	1.007
Final R indices [I > 2σ(I)]	R1 = 0.1048, wR2 = 0.2359
R indices (all data)	R1 = 0.2608, wR2 = 0.3486
Max electron density/e· Å^{-3}	1.364
Min electron density/e· Å^{-3}	-1.263

Table S2. Selected bond lengths [Å] and angles [°] for $[Ru^{II}(bipy)_2(pic)]Cl\cdot 5.5H_2O$.

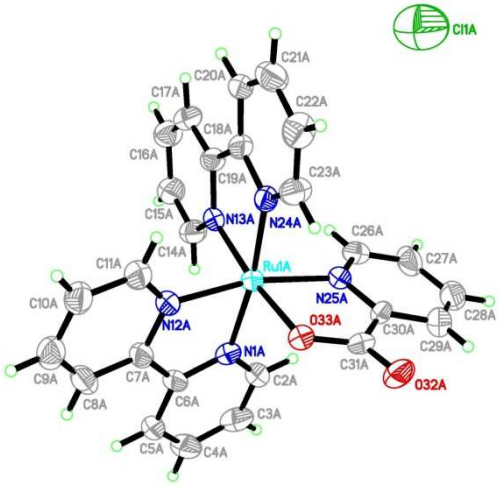
Bond lengths [Å]			
Ru1A-N1A	2.066(10)	Ru1B-N1B	2.038(9)
Ru1A-N12A	2.061(9)	Ru1B-N12B	2.067(9)
Ru1A-N13A	2.066(9)	Ru1B-N13B	2.074(9)
Ru1A-N24A	2.052(9)	Ru1B-N24B	2.053(9)
Ru1A-N25A	2.074(9)	Ru1B-N25B	2.3405(9)
Ru1A-O33A	2.107(8)	Ru1B-O33B	2.100(7)
Angles [°]			
N24A-Ru1A-N12A	95.8(4)	N24B-Ru1B-N12B	173.5(4)
N24A-Ru1A-N13A	79.7(4)	N24B-Ru1B-N13B	79.6(4)
N12A-Ru1A-N13A	92.7(3)	N12B-Ru1B-N13B	95.9(4)
N24A-Ru1A-N25A	91.9(3)	N24B-Ru1B-N25B	93.8(3)
N12A-Ru1A-N25A	166.9(4)	N12B-Ru1B-N25B	91.5(3)
N13A-Ru1A-N25A	99.1(3)	N13B-Ru1B-N25B	166.8(4)
N24A-Ru1A-N1A	172.3(3)	N24B-Ru1B-N1B	96.1(3)
N12A-Ru1A-N1A	79.0(4)	N12B-Ru1B-N1B	79.6(4)
N13A-Ru1A-N1A	94.9(4)	N13B-Ru1B-N1B	94.3(3)
N25A-Ru1A-N1A	94.3(4)	N25B-Ru1B-N1B	97.7(3)
N24A-Ru1A-O33A	93.8(3)	N24B-Ru1B-O33B	90.9(3)
N12A-Ru1A-O33A	90.8(3)	N12B-Ru1B-O33B	93.7(3)
N13A-Ru1A-O33A	172.9(3)	N13B-Ru1B-O33B	89.6(3)
N25A-Ru1A-O33A	78.1(3)	N25B-Ru1B-O33B	79.1(3)
N1A-Ru1A-O33A	91.9(3)	N1B-Ru1B-O33B	172.5(3)

The asymmetric unit of $[Ru^{II}(bipy)_2(pic)]Cl\cdot 5.5H_2O$ consists of two $[Ru^{II}(bipy)_2(pic)]^+$ cations, two Cl^- ions, and eleven water molecules (see Figure S1). The Ru(II) ions have a distorted octahedral geometry. Their coordination spheres are formed by two 2,2'-bipyridine ligands via their N atoms and one picolinate ligand via its N and O atoms. Pairs of nitrogen atoms of 2,2'-

bipyridine ligands are in *trans* positions, N1A and N24A for Ru1A, and N12B and N24B for Ru1B, analogously as in the mixed-valence Ru(II)-Ru(III) ion-pair complex. The architecture of the $[Ru^{II}(bipy)_2(pic)]^+$ ion is similar to that of the cation of the mixed-valence ion-pair complex.



(a)



(b)

Fig. S1. (a) Crystal structure of $[Ru^{II}(bipy)_2(pic)]Cl\cdot 5.5H_2O$ with the thermal ellipsoids plotted at 30% probability without labeling. (b) Crystal structure of $[Ru^{II}(bipy)_2(pic)]Cl\cdot 5.5H_2O$ with the thermal ellipsoids plotted at the 30% probability level. The solvent molecules (H_2O), Cl^- ion, and the second complex molecule are omitted for clarity.

The analysis of the $[Ru^{II}(bipy)_2(pic)]Cl\cdot 5.5H_2O$ structure revealed intermolecular C-H…N and C-H…O interactions. Also, a series of intra- and intermolecular O-H…O and O-H-Cl hydrogen bonds are detected (Table S3).

Table S3. Intra- and intermolecular interactions in $[Ru^{II}(bipy)_2(pic)]Cl \cdot 5.5H_2O$.

D-H…A	d(D-H)	d(H…A)	<DHA	d(D…A)
C2A-H2AA…N25A	0.930	2.698	116.36	3.221
C5A-H5AA…O33B[x+1/2,-y+3/2,z+1/2]	0.930	2.629	145.50	3.436
C14A-H14A…N1A	0.930	2.687	116.44	3.211
C17A-H17A…O32B [-x+1, -y+1, -z+1]	0.930	2.461	179.27	3.391
C20A-H20A…O32B[-x+1, -y+1, -z+1]	0.930	2.554	173.95	3.480
C23A-H23A…O33A	0.930	2.617	118.15	3.164
C29A-H29A…O32B[x+1/2,-y+1/2,-z+1/2]	0.930	2.583	150.59	3.424
C2B-H2BA…N24B	0.930	2.676	117.01	3.207
C5B-H5BA…O32A[-x+2,-y+3/2, z-1/2]	0.930	2.377	165.62	3.286
C23-H23A…N25B	0.930	2.700	115.88	3.217
C29B-H29B…O32A[x-1/2,-y+1/2,z-1/2]	0.930	2.545	151.48	3.391
O1W-H1C…O4W	0.859	2.135	164.36	2.972
O2W-H2B…O3W	0.834	2.318	148.63	2.972
O2W-H2B…O7W[x, y-1,z]	0.834	2.423	125.22	2.983
O4W-H4C…O2W	0.840	2.205	132.72	2.843
O5W-H5C…O6W	0.839	2.354	119.90	2.866
O5W-H5B…O7W	0.839	2.652	110.28	3.046
O6W-H6B…O8W	0.840	2.469	123.84	3.019
O7W-H7B…O3W[x,y+1,z]	0.841	2.341	145.68	3.072
O8W-H8C…O7W	0.856	2.132	158.54	2.946
O9W-H9C…O11W	0.774	2.496	114.97	2.909
O9W-H9B…O11W[-x+1,-y, -z]	0.776	2.175	168.01	2.938
O10W-H10D…Cl1A	0.849	2.412	163.35	3.235
O11W-H11C…O9W	0.763	2.287	139.43	2.908
O11W-H11D…Cl1B	0.766	2.346	120.93	2.817
011W-H11D…O10W	0.766	2.548	125.83	3.060

Additional structural information for the mixed valence ion-pair complex

Intermolecular interactions lead to the formation of the H-bonded dimer between two Ru(III) complex ions as shown in Figure S2.

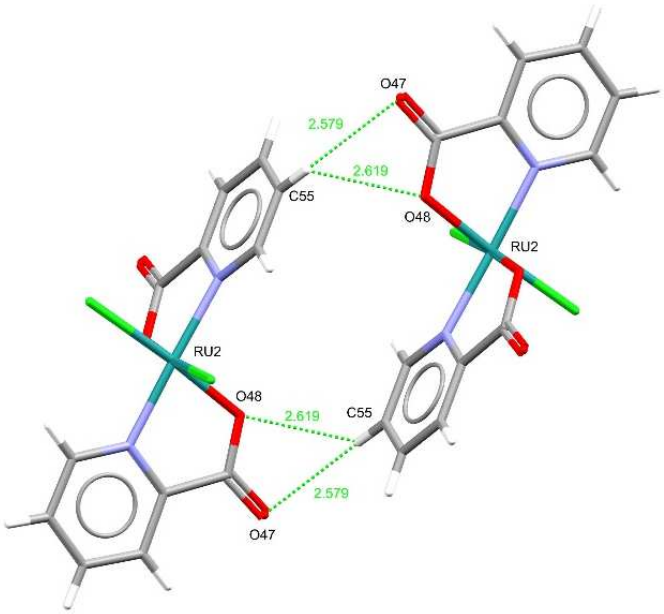


Fig. S2. Structure of the H-bonded dimer of two complex ions *cis*-$[Ru^{III}Cl_2(pic)_2]^-$ formed by intermolecular interactions C-H...O [-x+2, -y+2, -z+1].

Moreover, analysis of packing revealed the existence of H-bonds within π- π dimer between two Ru(III) complex ions, which is formed by intermolecular C-H...Cl interactions, with the C43-H43...Cl2 [1-x, 1-y, 1-z] distance being 2.767 Å (see Figure S3, *cf*. Figure 3).

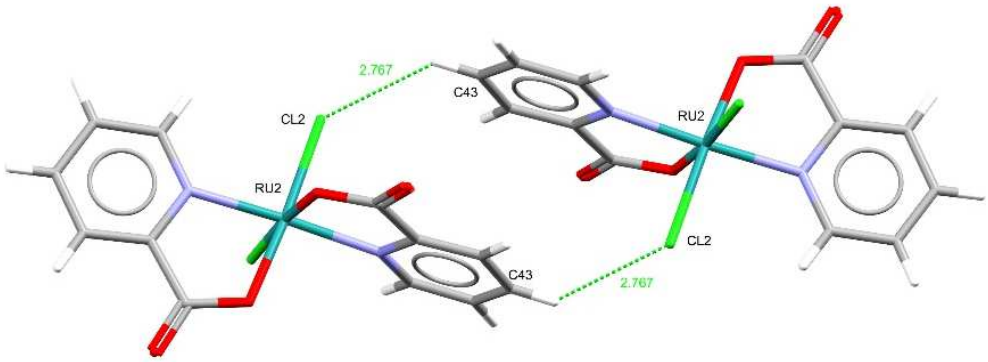


Fig. S3. Structure of the dimer of two complex ions *cis*-$[Ru^{III}Cl_2(pic)_2]^-$ formed by π-π and H-bond intermolecular interactions C43-H43...Cl2 [1-x, 1-y, 1-z].

The intermolecular π…π interactions are detected between 6-membered rings of two 2,2´-bipyridine ligands in the Ru(II) complex, with $\pi_{[N1--C6]}\ldots\pi_{[C7--N12]}$ [1-x, 2-y, 1-z] distance between the ring gravity centers being 3.7841(17) Å. There are C-H…π interactions between C11-H group of 2,2´-bipyridine ligand and pyridine ring (N13--C18), with C…π distance of 3.777(3) Å. The C-O…π interactions are also found in the Ru(III) complex, with the C50-O51…$\pi_{[N1--C6]}$ [1-x, 2-y, 1-z] distance of 3.763(3) Å.

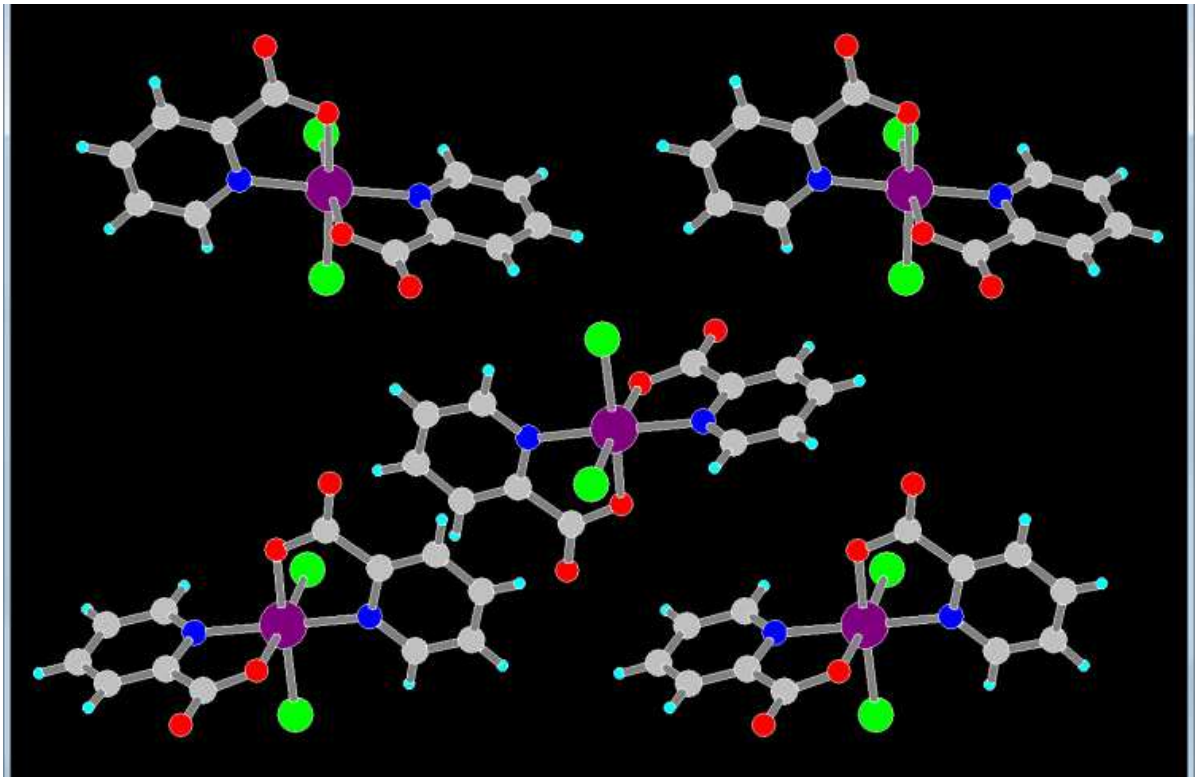


Fig. S4. Arrangement of the neighboring Ru(III) complex molecules. The Ru-Ru distances between the central unit and the bottom-left and bottom-right units are 8.699 and 7.250 Å, respectively. The two units at the bottom are related by the inversion center to the central one. The two upper units are related to the central one by C2 rotation with the Ru-Ru distance equal to 8.652 Å.

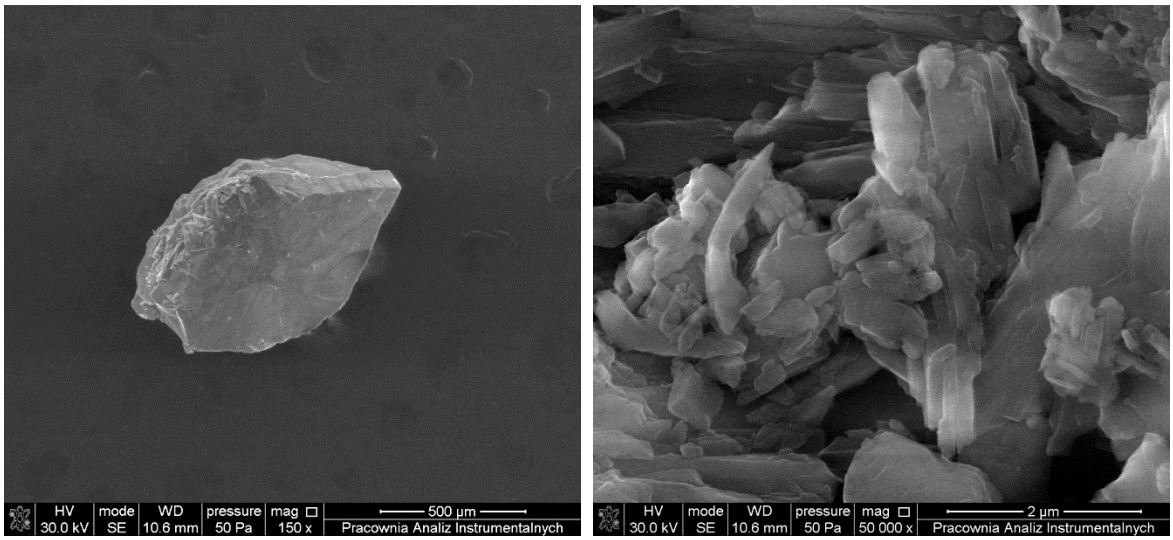


Fig. S5. SEM images of a crystal of the mixed-valence $[Ru^{II}(bipy)_2(pic)]^+[cis\text{-}Ru^{III}Cl_2(pic)_2]^-$ ion-pair at different resolutions.

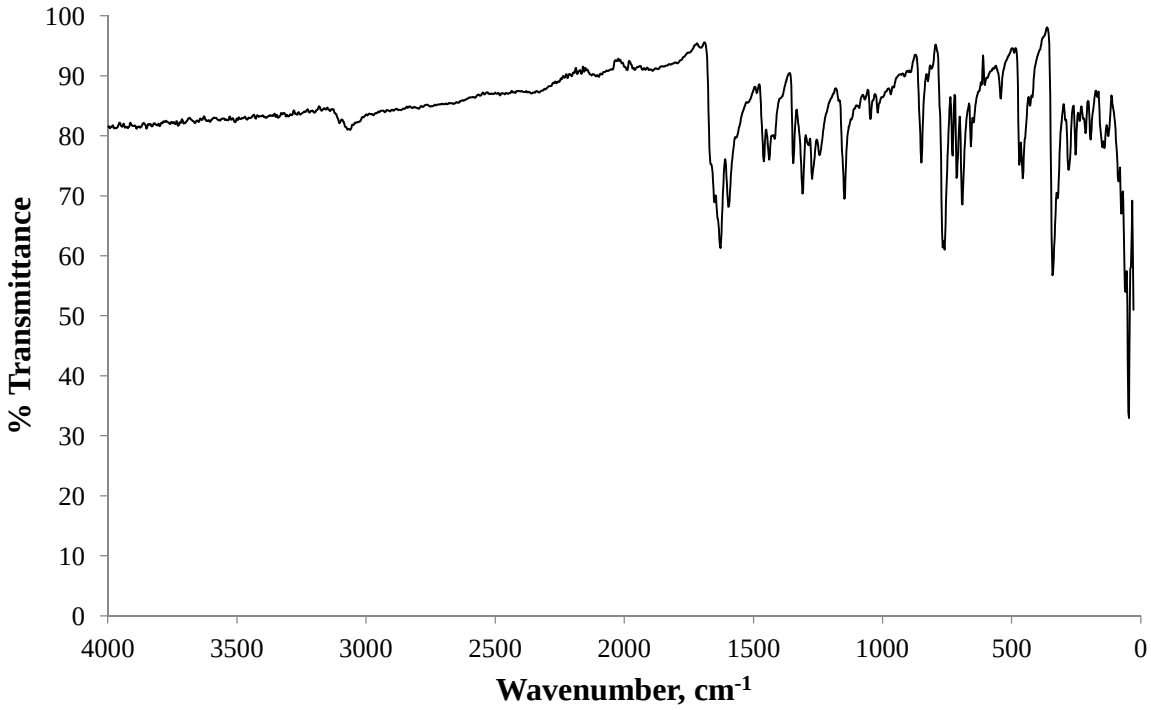
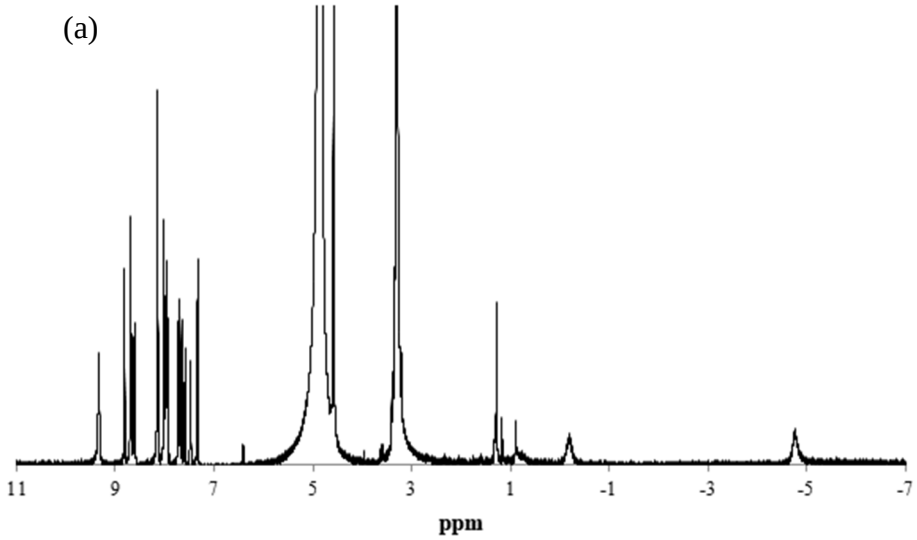
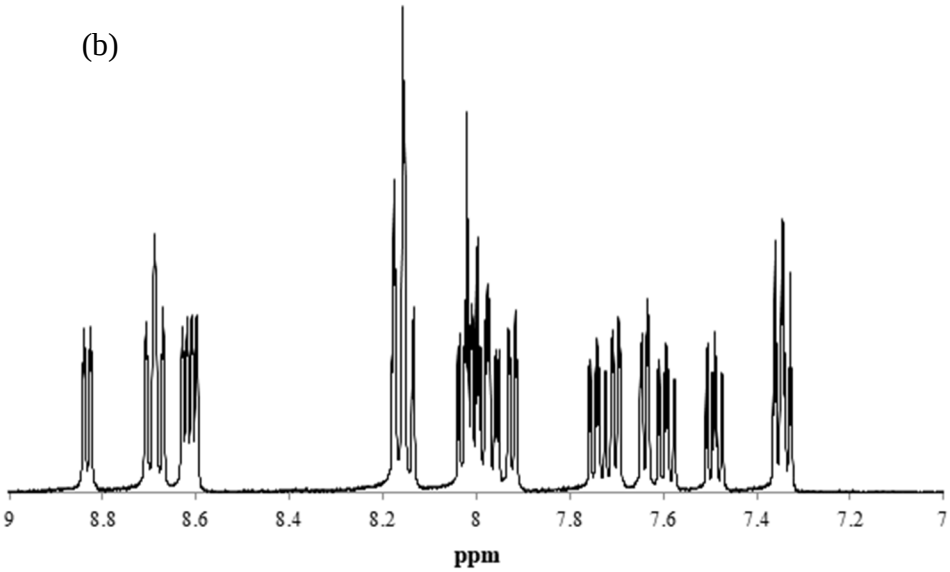


Fig. S6. IR spectrum for the mixed-valence $[Ru^{II}(bipy)_2(pic)]^+[cis\text{-}Ru^{III}Cl_2(pic)_2]^-$ ion-pair complex.

(a)



(b)



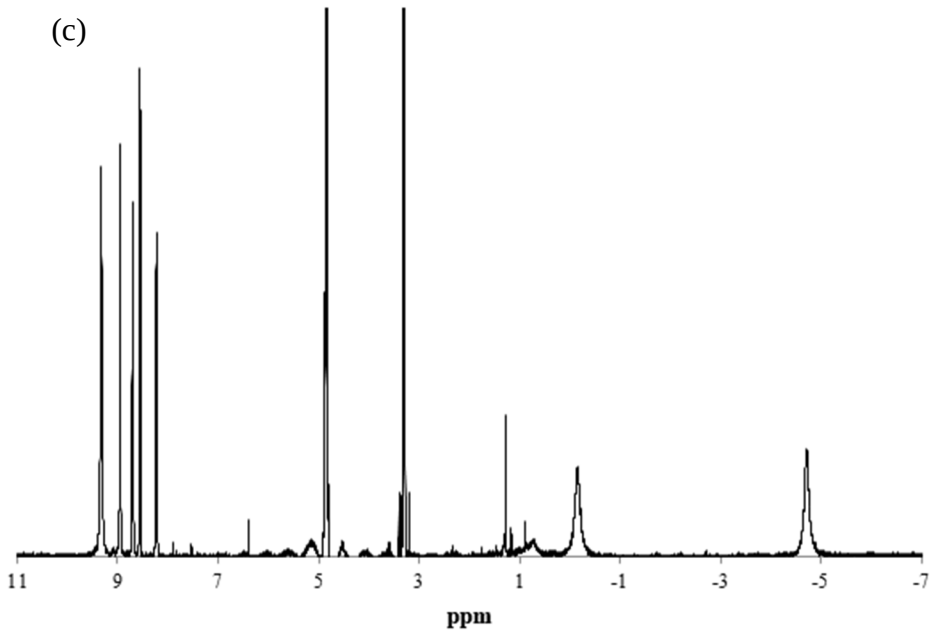


Fig. S7. ^{1}H NMR spectra of the mixed-valence $[Ru^{II}(bipy)_2(pic)]^+[cis\text{-}Ru^{III}Cl_2(pic)_2]^-$ ion-pair (a), $[Ru^{II}(bipy)_2(pic)]^+$ (b) and $cis\text{-}[Ru^{III}Cl_2(pic)_2]^-$ (c) complexes.

Table S4. XRD analysis of the mixed-valence Ru(II)/Ru(III) ion-pair complex (experimental and calculated data).

2θ [°]		2θ [°]	
Experimental	Calculated	Experimental	Calculated
12.04	12.00	19.54	19.50
12.68	12.60	20.00	20.00
13.70	13.62	20.64	20.58
14.32	14.26	21.30	21.18
15.20	15.16	22.24	22.22
15.90	15.82	23.96	23.84
16.78	16.74	24.36	24.22
18.00	17.94	26.34	26.28
19.08	19.16	28.40	28.34