Electronic Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry 2013

Supplementary materials

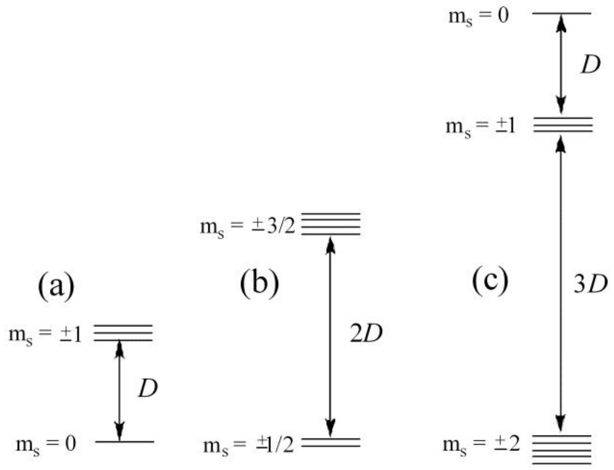
Diruthenium(III,III) Diphosphonate with a spin ground state *S* = 2

Bin Liu,[*,a,b] *Tuo Ding,*[a] *Wei-Jie Hua,*[c] *Xue-Mei Liu,*[a] *Huai-Ming Hu,*[a] *Li-Min Zheng,*[*,b] *Shu-Hua Li,*[*,c]

[a]Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an 710069, P. R. China

[b]State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China.

[c]Key Laboratory of Mesoscopic Chemistry of MOE, Institute of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China.



Scheme S1. Zero Field Splitting of $Ru_2(hedp)_2^{n-}$ [n = 4 (a), 3 (b) and 2 (c)]

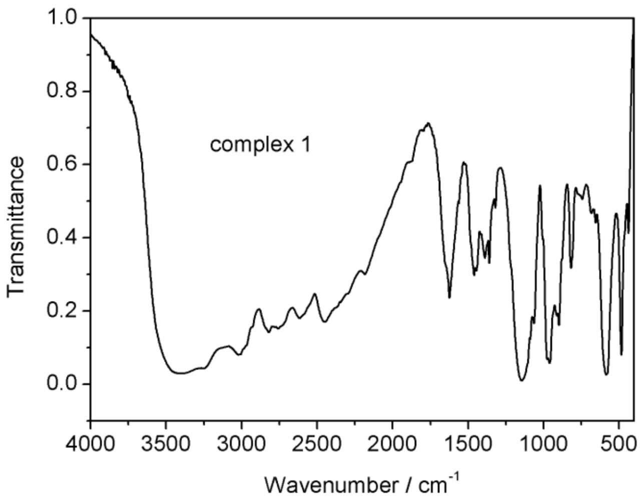


Figure S1. IR spectra of complex **1**

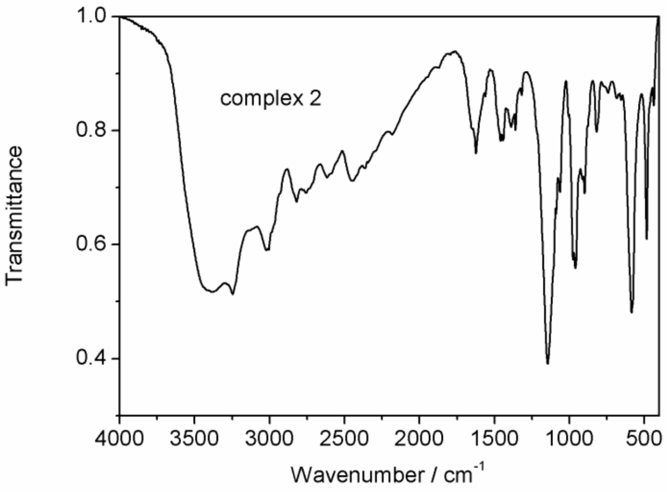


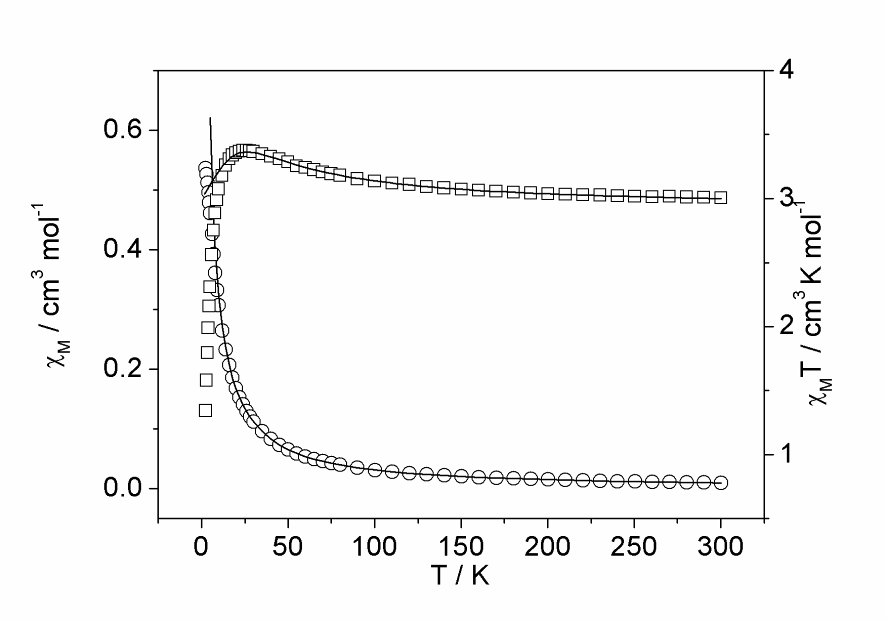
Figure S2. IR spectra of complex **2**

The zero-field splitting expression based on ground state S = 2.

$$\chi_z = \frac{2Ng_z^2\beta^2}{kT}\frac{1+4e^{-3D/kT}}{2+e^{D/kT}+2e^{-3D/kT}}$$

$$\chi_x = \frac{2Ng_x^2\beta^2}{3D}\frac{-7+9e^{D/kT}-2e^{-3D/kT}}{2+e^{D/kT}+2e^{-3D/kT}}$$

$$\chi = \frac{\chi_z+2\chi_x}{3} \qquad \chi'_M = \frac{\chi_M}{1-(2zJ/Ng'^2\beta^2)\chi_M} \qquad \text{where} \qquad g'^2 = \frac{g_z^2+2g_x^2}{3}$$



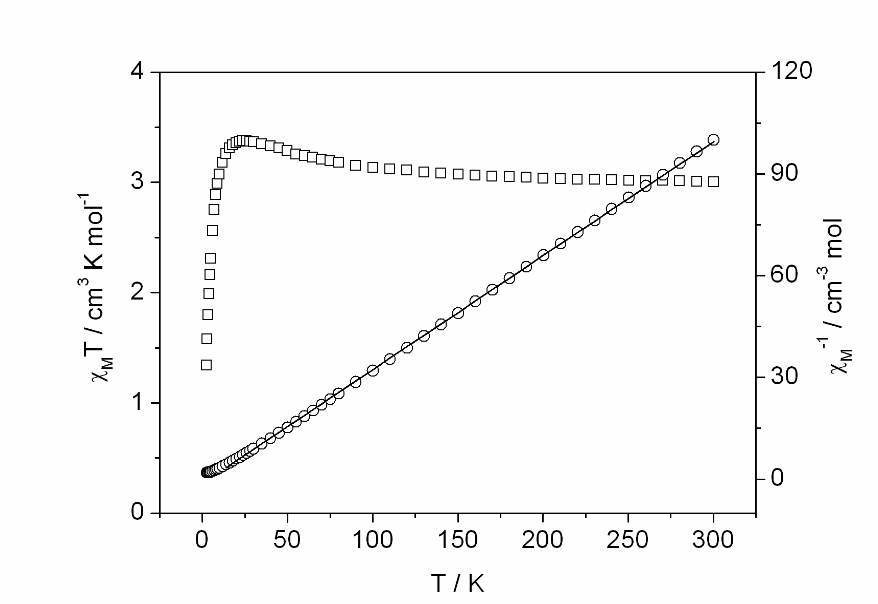


Figure S3. Temperature dependent magnetic susceptibilities of **1** recorded at 2 kOe. Solid line represents the best fitting of the data (see text for details).

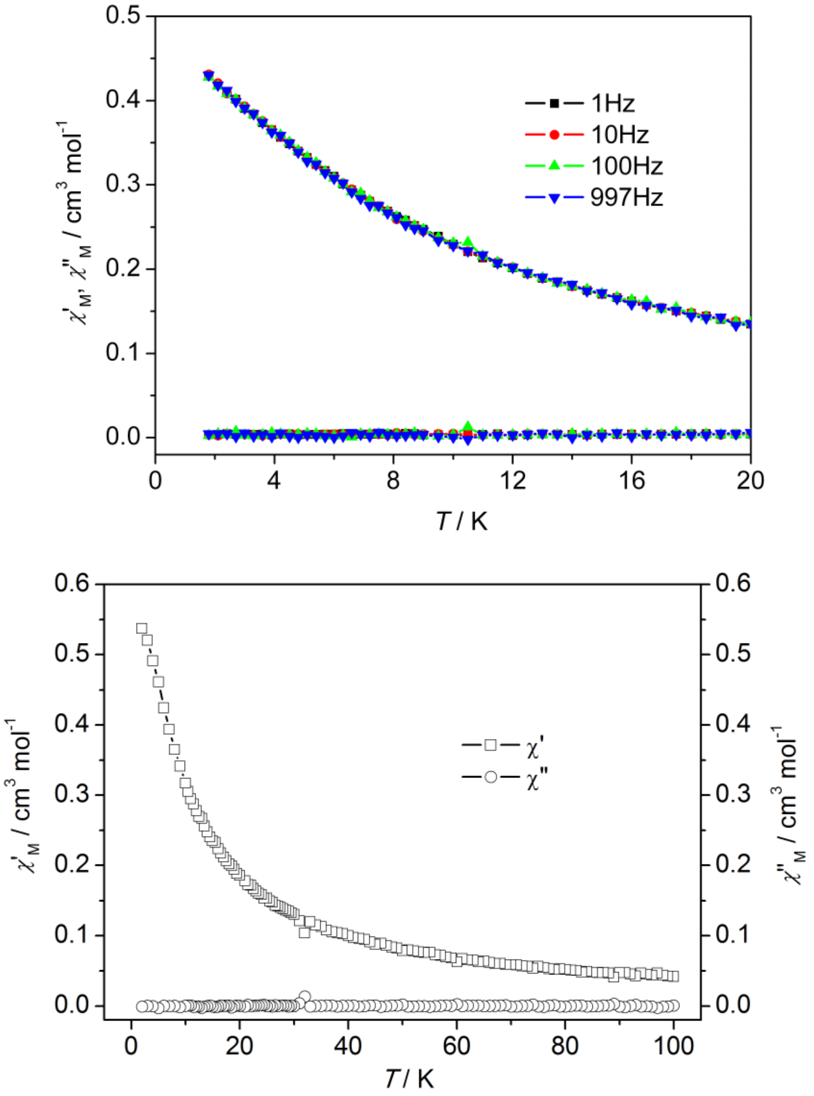


Figure S4. In-phase and out-of-phase ac magnetization component χ’ and χ’’ of **1** for frequency of 10 Hz between 1.8 and 100 K in the absence of a dc bias field.

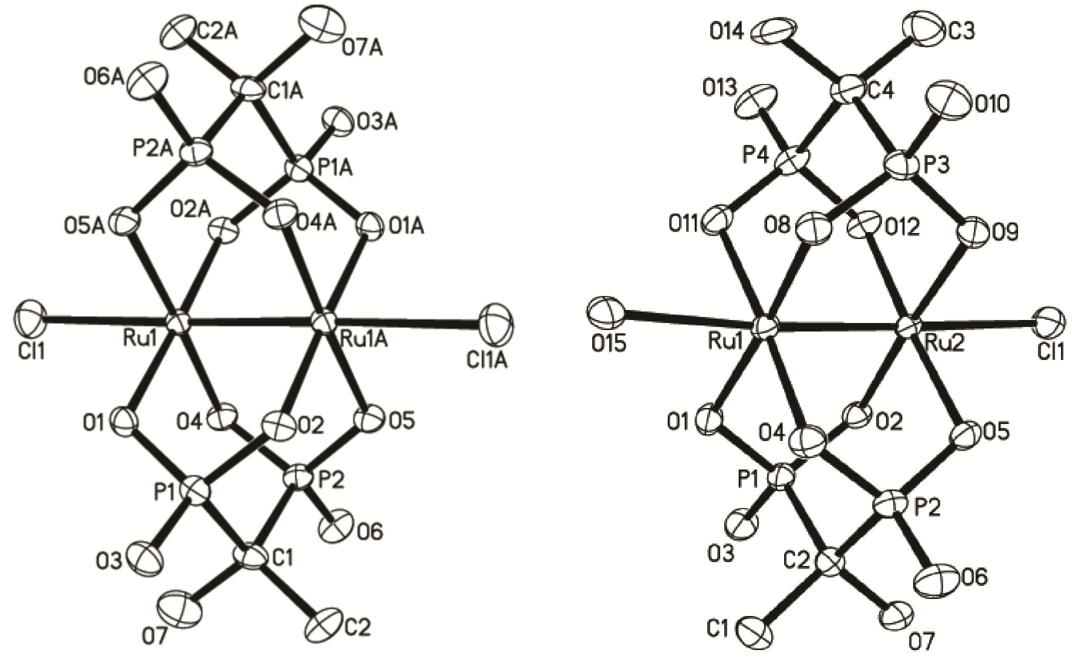
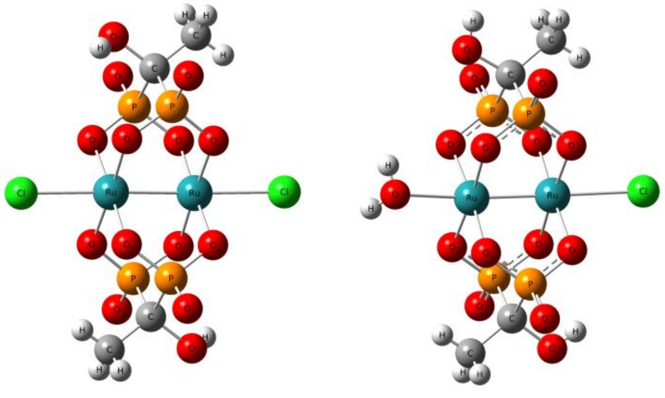
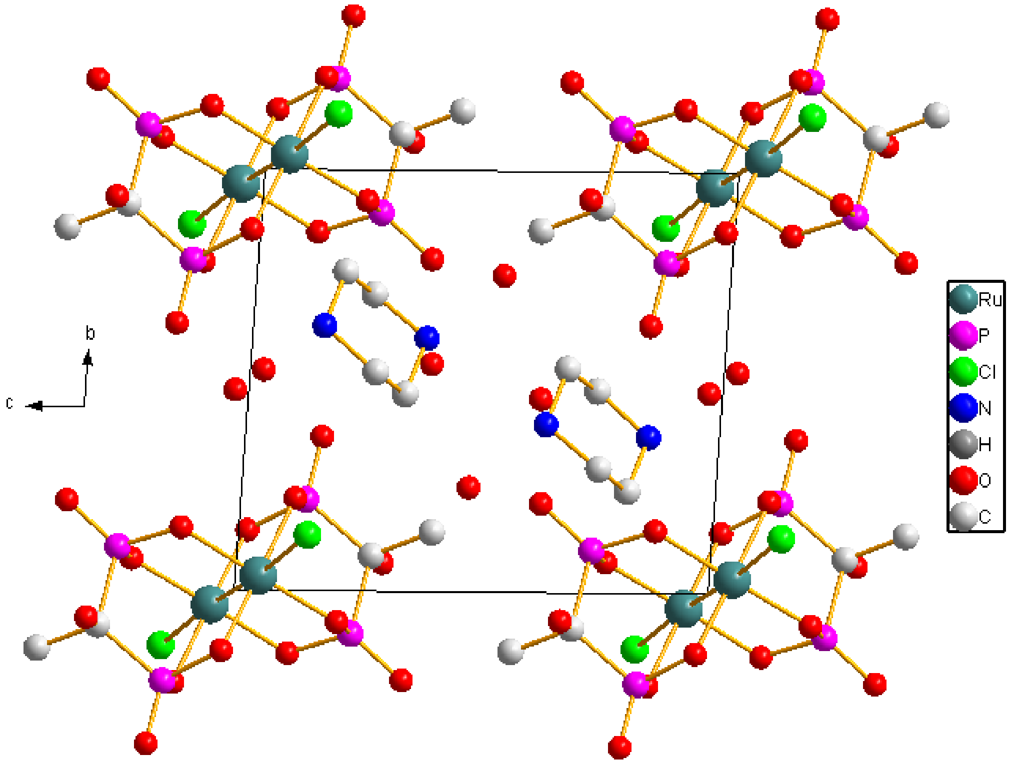


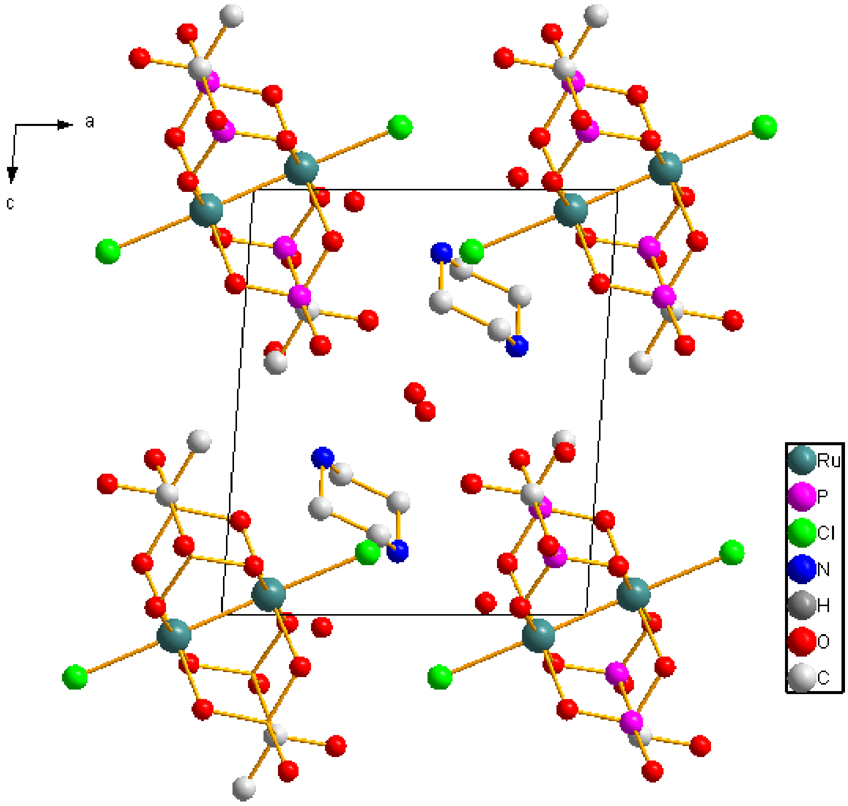
Figure S5. The $[Ru_2(hedp)_2Cl_2]^{4-}$ dimer in compound **1** and $[Ru_2(hedp)_2(H_2O)Cl]^{4-}$ in compound **2** with the atomic labeling scheme (thermal ellipsoids shown at 50% probability). All H atoms are omitted for clarity.


(a) Model **1**

(b) Model **2**

Figure S6. Calculation models for complexes **1** (a) and **2** (b).


b
c
Ru
P
Cl
N
H
O
C


a
c
Ru
P
Cl
N
H
O
C

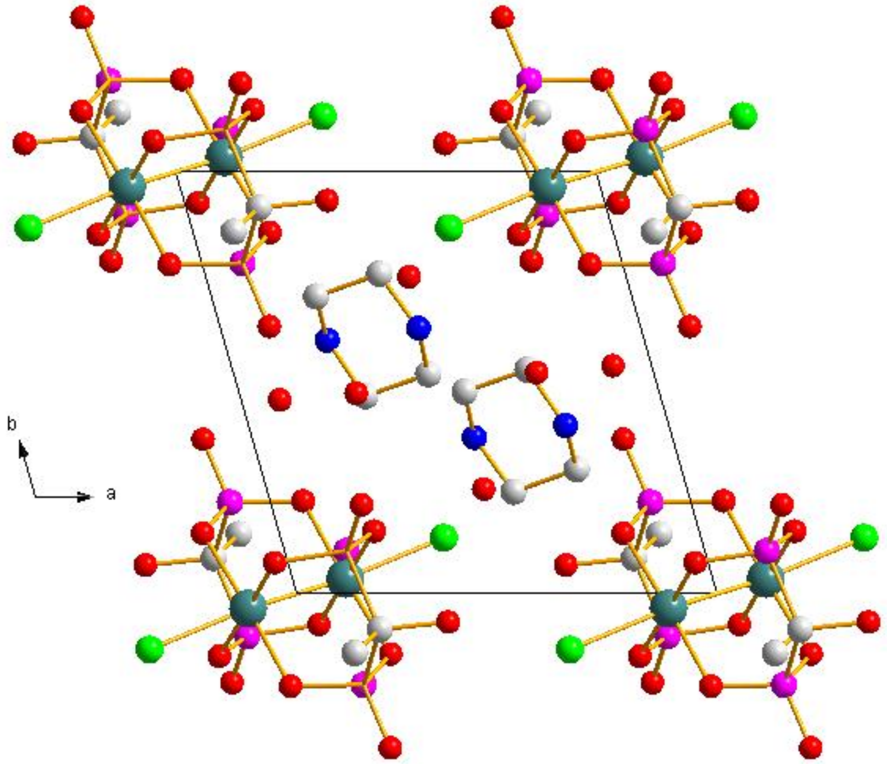
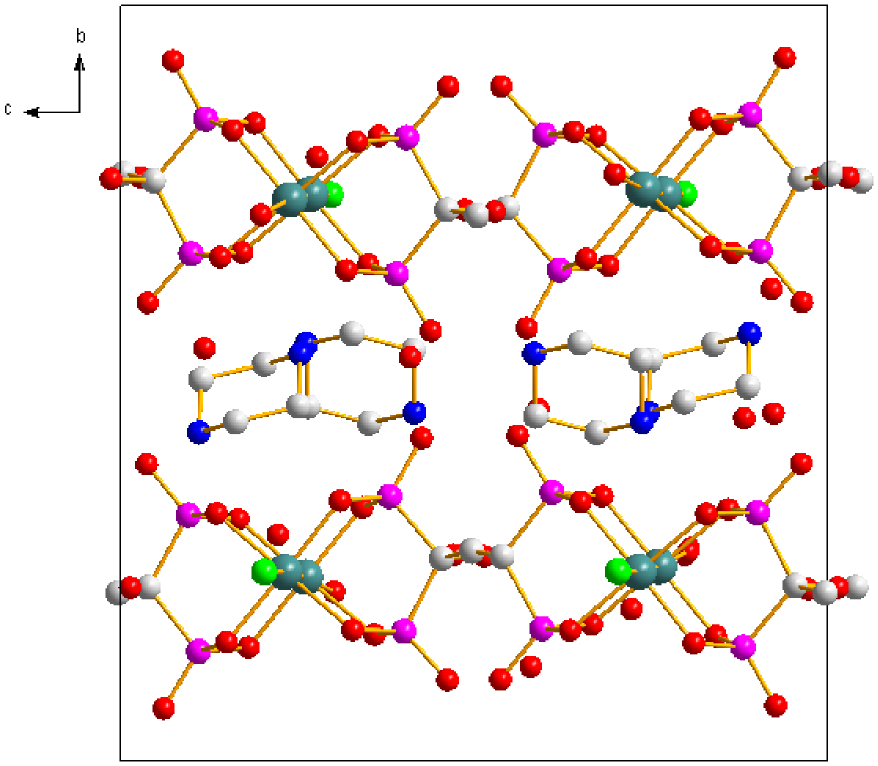


Figure S7. Projection of the crystal structure of **1** in the *bc*, *ac* and *ab* plane.



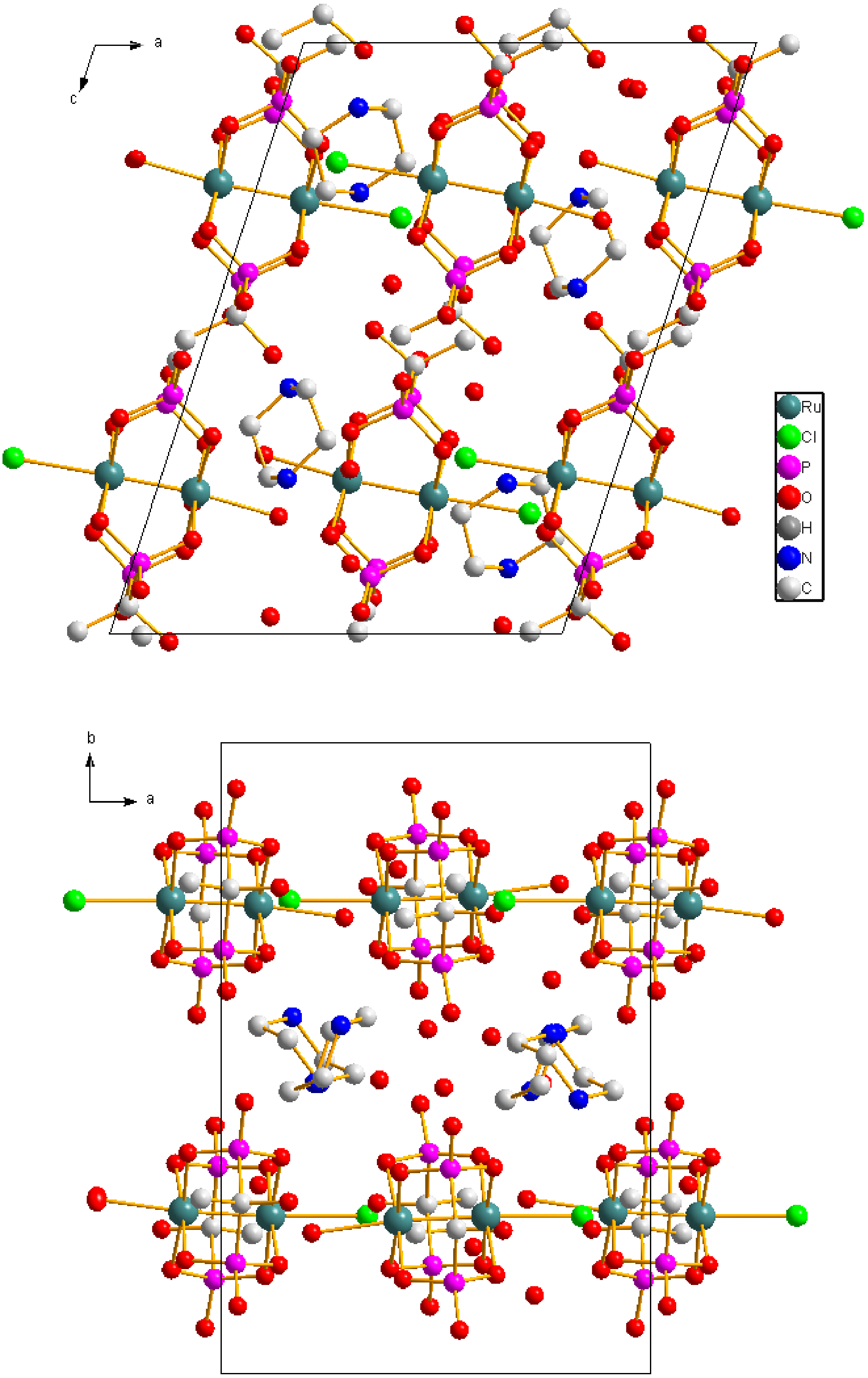
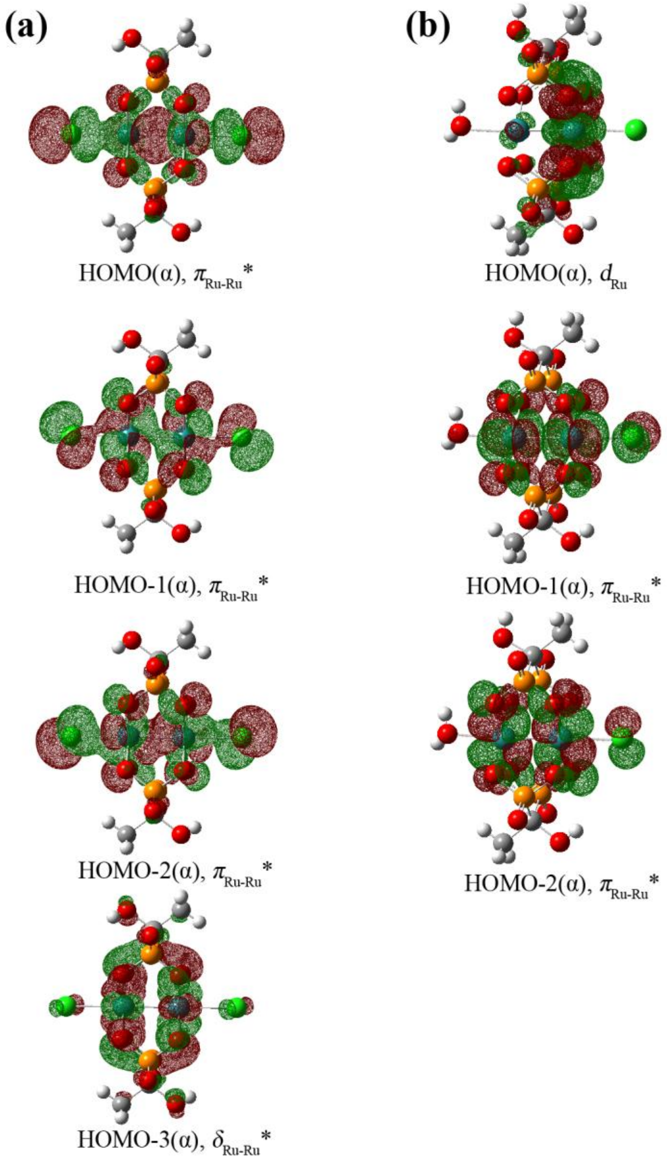


Figure S8. Projection of the crystal structure of **2** in the *bc*, *ac* and *ab* plane.

Electronic Structures via DFT Analysis



(a)

HOMO(α), $\pi_{\text{Ru-Ru}}{}^*$

HOMO-1(α), $\pi_{\text{Ru-Ru}}{}^*$

HOMO-2(α), $\pi_{\text{Ru-Ru}}{}^*$

HOMO-3(α), $\delta_{\text{Ru-Ru}}{}^*$

(b)

HOMO(α), d_{Ru}

HOMO-1(α), $\pi_{\text{Ru-Ru}}{}^*$

HOMO-2(α), $\pi_{\text{Ru-Ru}}{}^*$

Fig S9. Magnetic molecular orbitals in the ground states of complexes **1** (a) and **2** (b) calculated at the UB3LYP level.

To further understand the ground state spins, single point calculations are then carried out in different spin states at the unrestricted density functional theory (DFT) level with the B3LYP functional.[S1] For each complex, a cluster model is constructed by extracting the coordinated ligands around the $\text{Ru}_2{}^{n+}$ center from the crystal structure, as visualized in Figure S1 (denoted as models **1** and **2** for complexes **1** and **2**, respectively). In each calculation, a modified LANL2DZ basis set, with the optimized 5*p* functions[S2] and one *f*-type function[S3] is employed for ruthenium and the

6-31G** basis set for the other atoms. Besides, the LANL2DZ pseudo potential[S4] is also applied for ruthenium. All the calculations are performed by using the GAUSSIAN 03 package.[S5] As shown in Table S1 of the supporting information, we list the calculated energies and corresponding <S**2> values of two lowest spin states for models **1** and **2** (Figure S2). The ground state (GS) spins of complexes **1** and **2** have been verified to be S = 2 and S = 3/2 for complexes **1** and **2** respectively, which are in agreement with the magnetism measurement. The predicted separation between the GS and the lowest triplet (doublet) state is 0.3 eV (0.2 eV) for model **1** (model **2**). To better understand the metal-metal bonding, the magnetic molecular orbitals in the ground states of the two complexes are illustrated in Figure 4. For complex **1** with S = 2 (panel a), four singly occupied magnetic orbitals are one bonding σ-type orbital ($\sigma_{\text{Ru-Ru}}$), two π-type orbitals ($\pi_{\text{Ru-Ru}}$*) and one δ-type orbital ($\delta_{\text{Ru-Ru}}$*) of 4d orbitals on the two Ru atoms. It should be mentioned that the p orbitals from Ru-bound chlorine or oxygen atoms also make significant contributions to these four orbitals. While for complex **2** with S = 3/2 (panel b), three magnetic orbitals include one non-bonding 4d orbital on one Ru site (d_{Ru}) and two $\pi_{\text{Ru-Ru}}$* orbitals. One can see that the water ligand in complex **2** makes nearly no contribution to these orbitals.

Reference:

[S1] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785.

[S2] M. Couty and M. B. Hall, *J. Comput. Chem.* 1996, **17**, 1359.

[S3] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.* 1993, **208**, 111.

[S4] P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 299.

[S5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr. Montgomery, A. J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R.

Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, In Gaussian 03, Revision D.01; Gaussian, Inc.: Wallingford CT, 2004.

Table S1. Total energies and corresponding <S**2> values of low-lying spin states of models 1 and 2 calculated at the UB3LYP level.

multiplicity	E(a.u.)	<S**2>
model **1**		
triplet	-3684.023 32	3.03
quintet	-3684.035 05	6.02
model **2**		
doublet	-3300.134 57	1.77
quartet	-3300.141 97	3.76