Study of the interaction of water with the aqua-soluble dimeric complex [RuCp(PTA)$_2$-µ-CN-1κ*C*:2κ^2*N*-RuCp(PTA)$_2$](CF$_3$SO$_3$) (PTA = 1,3,5-triaza-7-phosphaadamantane) by Neutrons and X-ray diffraction in solution.

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Supporting Information

Materials and Methods

All chemicals were reagent grade and, unless otherwise stated, were used as received by commercial suppliers. All reactions were carried out in a pure argon atmosphere by using standard Schlenk-tube techniques with freshly distilled and oxygen-free solvents. The hydrosoluble phosphine-PTA and the complex [RuClCp(PTA)$_2$] were prepared as described in the literature.[1] ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H} NMR were routinely conducted on the Bruker DRX300 (300.13 MHz). The ^{1}H,^{1}H 2D COSY and ^{1}H,^{13}C{^{1}H} HSQC NMR experiments were routinely conducted on the same instrument in the absolute magnitude mode using a 45 or 90º pulse after the increment delay. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C{^{1}H}). Chemical shifts for ^{31}P{^{1}H} NMR spectra were measured relative to external 85 % H$_3$PO$_4$. Infrared spectra were recorded on KBr disks using a Bruker Vertex 70 FT-IR spectrometer. UV-vis spectra were obtained with a Jasco V-650 spectrometer from solutions of 10^{-3}-10^{-5} M in quartz cuvettes (1 cm optical path). Specific absorption coefficients were obtained by linear regression over 5-7 points (R^2 ≥ 0.999). Elemental analyses (C, H, N, S) were performed on a Fisons Instrument EA 1108 elemental analyzer.

Synthesis of 1(CF₃SO₃)

The complexe **1(CF₃SO₃)** was obtained by two different procedures:

Method A: [RuCpCl(PTA)₂] (250 mg, 0.484 mmol) was reacted with Ag(CF₃SO₃) (121 mg, 0.470 mmol) in 40 mL of MeOH/H₂O (2.5:1). After 1,5h at room temperature the resulting mixture was filtered through sintered glass with celite and its volume reduced until the elimination of the solvent. The obtained powder was added to a solution of [RuCp(CN-κC)(PTA)₂] (200 mg, 0.395 mmol) in 20 mL of a mixture MeOH/H₂O (2:1). The resulting solution was kept at 90ºC for 2h, cooled to room temperature and filtered. The solvent was completely evaporated and the resulting powder dissolved in 2 mL of EtOH. Addition of Et₂O (20 mL) precipitated a yellow powder, which was filtered, washed with Et₂O (3x10mL) and vacuum dried.

Method B: Similarly to the previous method, the complex [RuCpCl(PTA)₂] (250 mg, 0.484 mmol) was reacted with Ag(CF₃SO₃) (121 mg, 0.470 mmol) in 40 mL of MeOH/H₂O (2.5:1). After 1,5h at room temperature the resulting mixture was filtered through sintered glass with celite. Into the resulting solution was added KCN (15 mg, 0.230 mmol). After 2 hour at 90 ºC the solution was cooled, filtered through sintered glass and its volume reduced until the elimination of the solvent. The obtained residue was dissolved in 2 mL of EtOH. Addition of 20 mL of Et₂O gave rise to a yellow-orange precipitate that was filtered, washed with Et₂O (2 x 2 mL) and air dried. Crystals suitable for single crystal X-ray diffraction were obtained from a concentrated dissolution in H₂O/DMSO (1:1). Power yield: 0.406 g, 82%. $S_{25}(mg/cm^3)$: 320. Elemental analysis for $C_{36}H_{76}ClN_{13}O_9P_4Ru_2$ (1184.55): Found C, 35.53; H, 6.27; N, 15.59. Calcd. C, 35.49; H, 6.47; N, 15.37. IR (KBr): ν = 2113 cm⁻¹ (μ-N≡C); ν = 2057 cm⁻¹ (μ-C≡N); 1280, 1241, 1167, 1099 ν(OSO+C-N). ¹H NMR (300,13 MHz, 23 º C, TMS, D₂O): δ = 3.85-3.97 (m, 24 H, NCH₂P); 4.38-4.50 (m, 24 H, NCH₂N); 4.80, 4.94 (s, s, Cp). ³¹P{¹H} NMR (121.49 MHz, 23 ºC, 85 % H₃PO₄, D₂O): δ = -19.35 (s, PTA$_{Ru-NC}$), -21.97 (s, PTA$_{Ru-CN}$). ³¹C{¹H} NMR (75.467 MHz, 23 ºC, TMS, D₂O): δ = 56.38 (t, $^1J_{CP}$ = 9.51 Hz, NCH₂P), 70.75 (s, NCH₂N), 77.57 (s, Cp$_{Ru-NC}$), 80.16 (s, Cp$_{Ru-CN}$), 151.94 (m, CN). UV/Vis (H₂O, 5x10⁻⁴ mol/L) λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹): 314 (2905), 222 (9723). UV/Vis (DMSO, 5x10⁻⁴ mol/L) λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹): 321 (3515), 260 (4896).

X-ray crystal structure experimental details for complex 1(CF₃SO₃)·6H₂O

Yellow-orange crystals of **1** were obtained by slow evaporation of its dissolution in H_2O/DMSO. Crystal data for **1**, $C_{35}H_{76}ClN_{13}O_9P_4Ru_2$, Triclinic, space group *P-1* (no. 2), *a* = 14.5313(7), *b* = 17.5256(8), *c* = 18.3097(9), α = 66.9270(10), β = 73.1200(10), γ = 76.5130(10), *V* = 4067.1(3) Å³, *Z* = 1, ρ_{calcd} = 1.429 g.cm⁻³, final R_1 value 0.0569 for 14015 independent reflections ($I > 2\sigma(I)$). The data collections were performed at 100 K on a Bruker APEX CCD area detector diffractometer, using MoK_α radiation (λ = 0.71073 Å) by the *ω* scan method, within the limits $4.722 < \theta < 49.958°$. Empirical absorption correction was applied with T_{min} = 0.855 and T_{max} = 0.889. The structure was solved by direct methods (SIR97) and refined by full matrix least squares on F^2 (SHELX 97).[2] Anisotropic thermal factors were assigned to all the non-hydrogen atoms. All the H atoms were placed in calculated positions and not refined. All the diagrams were generated by using the SHELXL program. **CCDC 1000027** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the World Wide Web (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033 or emailing deposit@ccdc.cam.ac.uk).

Table S1. Selected crystallographic data for **1(CF₃SO₃).6H₂O**

	1(CF₃SO₃)·6H₂O
Empirical formula	$C_{35}H_{76}ClN_{13}O_9P_4Ru$
Formula weight	1184.55
Crystal dimensions (mm³)	0.200x0.170x0.150
Crystal system	Triclinic
Space group	P-1
a[Å]	14.5313(7)
b[Å]	17.5256(8)
c[Å]	18.3097(9)
α [deg]	66.9270(10)
β [deg]	73.1200(10)
γ [deg]	76.5130(10)
Z	3
Volume [Å³]	4067.1(3)
$\rho_{calcd.}$ [mg·cm⁻³]	1.429
μ [mm⁻¹]	0.781

F(000)	1788
Data/Restrains/Parameters	14015 / 3 / 940
R1 [I>2σ(I)] (all)	0.0569 (0.0640)
wR2 [I>2σ(I)] (all)	0.1679 (0.1767)
GOF	1.062
Δρ[e·Å³]	2.841; -0.849

Average of Selected bond distances (Å) and angles (°) for complex 1.

Ru-P 2.258(5); Ru-N(C) 2.018(10); Ru1-Cp$_{(centroid)}$ 1.874(4); N$_{CN}$-C$_{CN}$ 1.145(8); P-Ru-P 95.09(1.29); N(C)-Ru-P 85.99(2.70).

Single crystal structure and main properties discussion of 1(CF$_3$SO$_3$)6H$_2$O.

Slow crystallization in air of a H$_2$O/DMSO solution of **1** gave yellow-orange crystals suitable for single crystal X-ray diffraction data collection.[3] The asymmetric unit cell of **1** in the solid state is constituted by 6 disordered water molecules, three CF$_3$SO$_3^-$ anions and three binuclear-cationic-complex in which two piano-stool-{CpRu(PTA)$_2$} moieties are linked by a disordered CN$^-$ ligand (73/27 %) that links both metals to each other (Figure 1). Selected bond lengths and angles are provided in the Supporting Information. Both Cp and PTA ligands are in opposite directions as imposed by the "i" symmetry element at the middle of the C-N bond length (Ru-CN(NC) = 2.012(5) Å; C≡N = 1.137(9) Å; Ru-CN(NC) = 2.028(5) Å; C≡N = 1.151(10) Å). The Ru-CN-Ru bond lengths in **1**

are similar to those found for Cp-ruthenium complexes containing coordinate CN^- and,[4] most interestingly, in the complex $\{[\{(PTA)_2CpRu-\mu-CN-RuCp(PTA)_2\}-\mu-Au(CN)_4]\}_n$ (Ru-CN-Ru-Au).[3] The coordination geometry around ruthenium is more regular, with the Ru-Cp$_{(centroid)}$ distance (average: 1.874(4)Å) while the Ru-P separation is (average: 2.2584(54) Å).

The IR of $\mathbf{1(CF_3SO_3)6H_2O}$ shows absorption bands for both Ru-NC (2113 cm^{-1}) and Ru-CN (2057 cm^{-1}) coordinated bridged ligand. The stretching frequencies ascribable to the Ru-CN bonded to Ru are somewhat similar (3 cm^{-1}) to that of the cyano-ligand in the complex $[RuCp(CN-\kappa C)(PTA)_2]$ (2060 cm^{-1}) and different to the unique band observed for the polymeric complex Ru-CN-Ru-Au (2097 cm^{-1}).[3] In general, the absorption of bridging cyano-groups is similar to that for parent bi-nuclear cyano-complexes.[5] Complex $\mathbf{1}$ is characterized by two singlet signals at -19.35 (PTA-Ru-N) and -21.97 (PTA-Ru-C) in $^{31}P\{^1H\}$ NMR (D$_2$O) that are close to that observed for the polymer Ru-CN-Ru-Au (-19.21 and -21.82 ppm). The ^1H NMR shows multiplets between 3,85 – 3,97 (PTA$_{NCH_2P}$) and 4,38 – 4,50 (PTA$_{NCH_2N}$) and, more interestingly, two signals at 4.80 (Cp) and 4.94 (Cp) that have similar chemical shifts to the polymer Ru-CN-Ru-Au (4.80 and 4.95 ppm Ru-Cp ligands),[6] while they appear in the $^{13}C\{^1H\}$ NMR at 77.57 ppm ($\mathbf{Cp}$-RuNC) and 80.16 ppm ($\mathbf{Cp}$-RuCN), and the CN at 151.94 ppm ($\mathbf{CN}$).

Experimental details for Neutron diffraction and EPSR simulation of neutron and X-ray diffraction data of $\mathbf{1(CF_3SO_3).6H_2O}$ in water

For the neutron experiment complex $\mathbf{1(CF_3SO_3)6H_2O}$ has been dissolved at 0.1M concentration in H$_2$O, D$_2$O and an equimolar mixture of the two (labelled HDO). The three solutions have then been transferred in flat TiZr alloy cans at 25ºC (sample thickness 1mm). X-rays measurements have been performed on a sample at the same concentration in H$_2$O, in a 1 mm fused quartz capillary tube. The neutron experiments have been performed on the SANDALS diffractometer at the ISIS spallation neutron source, located at the Rutherford Appleton Laboratory (United Kingdom). The neutron data have been corrected for detectors efficiency, attenuation, multiple scattering, and inelastic scattering using well established methods.[18a] White beam X-ray diffraction

data have been collected on a Panaytical Ag-source diffractometer also available at ISIS. High-energy X-ray data were corrected for detector efficiency, polarization, Compton scattering and fluorescence.[18a,b] Computational models of the system have been obtained through Empirical Potential Structure Refinement (EPSR).[19a,b] The algorithm is based on a classical Monte Carlo simulation of the molecular system under study at fixed concentration and density, and employs an iterative algorithm that aims at building an atomistic three dimensional model consistent with the scattering data. The simulation box contains four molecules of **1**, four $CF_3SO_3^-$ anions and 2000 water molecules. The reference potential and molecular structure of **1** have been determined from the ab initio atomic structure in the gas phase and from the corresponding Mulliken population charges, both computed at the B3LYP level of DFT.[7] For trilflate molecules they have been calculated via MOPAC energy minimisation routine, included in the EPSR distribution, while for water molecules the standard and proved SPC/E model has been adopted.[19c] Spatial Density Functions (SDF)[17] are calculated within EPSR with respect to a frame of reference attached to complex **1** in the following way: the Ruthenium atom (attached to central carbon) is represented as a green sphere at (0,0,0), with z axis coming through the middle of the five carbon atoms on the Cp group and the x axis going through one of these carbon atoms (the distribution has 5 fold symmetry by construction). After fixing the orientation of a central molecule in a Cartesian frame of reference, the positions of the other molecules between a minimum and a maximum radius are calculated as a function of the elevation angle theta and the azimuthal angle phi. The procedure is repeated for all the molecules in the box and for an ensemble of configurations.

Table S2. Parameters for the reference (seeding) potentials for EPSR simulations, in the form of Lennard-Jones potential depth ε and radius σ, plus Coulombic partial charge q. The parameters have been derived from various sources: Complex 1 (from ab initio, see main text), triflate (from MOPAC minimisation, embedded into EPSR simulation) and water (SPC/E). Details of molecular structure (bond lengths, angles and dihedral angles) for all molecules are available upon request.

Symbol	Atom type	L-J ε[kJ/mol]	L-J σ[Å]	Charge q [e]
CC	central C	0.8	3.7	0.1600
NN	central N	0.7	3.2	-0.5800
Ruc	Ru(-C)	0.8	3.2	0.5000
Run	Ru(-N)	0.8	3.2	0.4900
Cp	C (Cp)	0.8	3.7	-0.2800
Hp	H (Cp)	0.0	0.0	0.2100
P	P (PTA)	0.8	3.2	0.8924
Cb1	C (-P, PTA)	0.8	3.7	-0.6526
Hb1	(-C-P, PTA)	0.0	0.0	0.2713
Nb	N (PTA)	0.7	3.2	-0.4683
Cb2	C (-N, PTA)	0.8	3.7	-0.1300
Hb2	H (-C-N, PTA)	0.0	0.0	0.2525
Ot	O (triflate)	0.65	3.1	-1.0233
St	S (triflate)	0.8	3.2	2.8607
Ct	C (triflate)	0.8	3.7	-0.1260
Ft	F (triflate)	0.8	3.2	-0.2216
OW	O (water)	0.65	3.166	-0.8476
HW	H (water)	0.0	0.0	0.4238

Figure S1 Structure factors from neutron and X-rays diffraction experiments (empty circles). EPSR calculation for the structure factors (line). Details of both techniques can be obtained from ref. 18a,b.
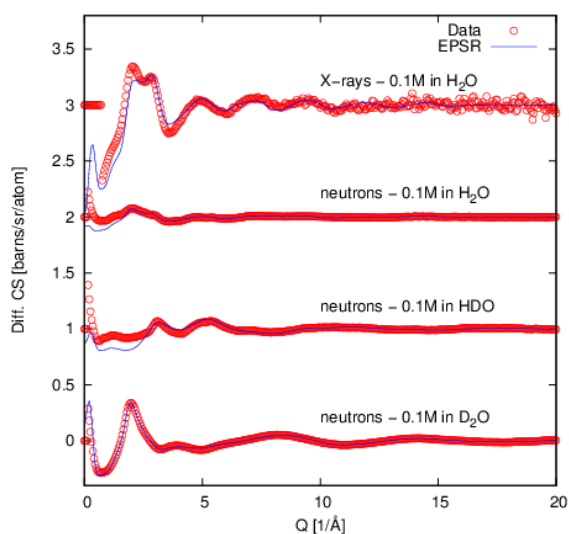
Experimental details for theoretical calculations of 1

Density-Functional Theory (DFT) calculations at the B3LYP[8] level of theory were carried out using NWChem 6.1.1.[9] A Gaussian basis set expansion of the Kohn-Sham orbitals of 3-21G quality was used in all calculations. UV absorption spectra were computed using TD-DFT (at the TD-B3LYP level). UV absorption spectra were obtained by convoluting the 60 lowest singlet excitation energies obtained from the iterative (Davidson) solutions of the TD-DFT equations with a Gaussian distribution of FWHM=10 nm. For the gas phase complex, the TD-DFT calculations were carried out on the optimised geometry, whereas atomic configurations obtained from EPSR simulations were used to model the solvation environment. In the latter case, only water molecules within a sphere of radius r=9 angstrom were included in the calculation. No relaxation of the atomic positions relative to the EPSR reference coordinates was allowed in this case.

Coupling DFT/TD-DFT calculations with classical force-field (EPSR) simulations is indeed one of the most innovative and technically challenging aspects of our work, to which we have devoted considerable work over the last three years. Our approach is based on a ``self-consistent'' procedure (details of which will appear in

future publications), which starts with a DFT calculation on the isolated organometallic complex in the gas phase. From this calculation we obtain atomic charges (e.g. Mulliken charges, see Supporting Information) and these are then used to parameterise an initial force field for the EPSR simulations. The potential is then refined in the course of the EPSR runs, to obtain pair correlation functions (PCFs), which can then be used to interpret the solvation shell structure of the solute. At least in principle there is a unique set of PCFs that are consistent with a given solvent structure. One of the innovative aspects of our work is then to use a set of instantaneous EPSR atomic configurations (not the PCFs themselves) of the solvated complex for the refined EPSR force field to perform DFT/TD-DFT calculations on ``micro-solvated'' samples (i.e. the complex surrounded by a few shells of water molecules, with the atomic position clamped to their EPSR values). The DFT calculations are not guaranteed to converge for a generic classical force-field atomic geometry. Our prescription provides EPSR geometries that are consistent with DFT (in virtue of the use of the DFT Mulliken charge constraint) and therefore pose less severe convergence problems.

Table S3. Atomic positions (in angstrom) for the isolated gas-phase complex 1

Ru   19.84799   13.93531   17.35630

P   19.84411   11.97398   16.23903

P   19.16319   15.12597   15.56930

N   19.97924   9.22018   16.39356

N   20.94497   10.24761   14.38616

N   18.52079   10.13686   14.65326

N   19.37625   15.77047   12.88346

N   17.20125   16.18021   13.90438

N   19.11265   17.65000   14.41401

C   20.03927   10.45717   17.23422

H   20.90972   10.48719   17.70616

H	19.32461	10.42118	17.91755
C	21.12046	11.59065	14.95151
H	21.06122	12.26029	14.22556
H	22.02128	11.65783	15.35627
C	18.34408	11.45451	15.26778
H	17.55703	11.43182	15.86918
H	18.16592	12.12409	14.55986
C	21.06263	9.20182	15.40379
H	21.92705	9.31049	15.87574
H	21.07308	8.31897	14.95642
C	19.64161	10.09406	13.74706
H	19.53216	10.81148	13.07356
H	19.62408	9.22699	13.26528
C	18.71948	9.14188	15.67254
H	18.65693	8.24922	15.25303
H	17.98172	9.21443	16.32802
C	19.85136	14.76564	13.88963
H	20.84134	14.78241	13.93060
H	19.57132	13.85845	13.60777
C	19.71540	17.16200	13.24890
H	20.69826	17.22636	13.35541
H	19.46124	17.75275	12.49509
C	19.59901	16.92339	15.65287
H	19.18623	17.32704	16.45747
H	20.58142	17.02039	15.72989

C   17.95542   15.71051   12.83430

H   17.66586   16.20663   12.02806

H   17.70561   14.76261   12.69174

C   17.61839   17.55292   14.25506

H   17.18112   17.82273   15.10063

H   17.32186   18.17672   13.54550

C   17.41585   15.27552   15.11865

H   17.05488   14.37570   14.92037

H   16.91307   15.64139   15.88884

C   20.25171   14.71366   19.39730

H   21.07123   15.13674   19.62344

C   19.14167   15.37301   18.92044

H   19.02677   16.30364   18.76640

C   18.16413   14.27121   18.70086

H   17.28465   14.36696   18.35673

C   18.75268   13.09819   19.08267

H   18.34438   12.24003   19.05645

C   20.01894   13.36279   19.50546

H   20.63980   12.71849   19.82336

N   22.68668   14.53575   16.16742

C   21.71546   14.27922   16.60659

Ru 24.55415   14.87966   15.41772

P   24.55804   16.84099   16.53498

P   25.23896   13.68900   17.20472

N   24.42290   19.59478   16.38045

N   23.45717   18.56736   18.38786

N   25.88135   18.67811   18.12075

N   25.02589   13.04450   19.89055

N   27.20089   12.63475   18.86964

N   25.28949   11.16497   18.36000

C   24.36287   18.35780   15.53980

H   23.49242   18.32778   15.06785

H   25.07753   18.39379   14.85646

C   23.28168   17.22432   17.82251

H   23.34092   16.55468   18.54846

H   22.38086   17.15714   17.41775

C   26.05806   17.36046   17.50624

H   26.84511   17.38314   16.90484

H   26.23622   16.69087   18.21416

C   23.33951   19.61315   17.37023

H   22.47509   19.50448   16.89828

H   23.32906   20.49599   17.81760

C   24.76053   18.72091   19.02696

H   24.86998   18.00349   19.70046

H   24.77806   19.58798   19.50873

C   25.68266   19.67309   17.10148

H   25.74521   20.56575   17.52099

H   26.42042   19.60053   16.44600

C   24.55078   14.04933   18.88439

H   23.56080   14.03256   18.84342

H 24.83082 14.95652 19.16624

C 24.68674 11.65297 19.52512

H 23.70388 11.58861 19.41861

H 24.94090 11.06221 20.27892

C 24.80313 11.89158 17.12115

H 25.21591 11.48793 16.31655

H 23.82072 11.79458 17.04413

C 26.44672 13.10446 19.93971

H 26.73628 12.60834 20.74595

H 26.69653 14.05236 20.08228

C 26.78375 11.26205 18.51896

H 27.22102 10.99224 17.67339

H 27.08028 10.63825 19.22852

C 26.98629 13.53945 17.65536

H 27.34726 14.43927 17.85365

H 27.48907 13.17358 16.88517

C 24.15043 14.10131 13.37671

H 23.33091 13.67823 13.15057

C 25.26047 13.44195 13.85358

H 25.37537 12.51132 14.00762

C 26.23801 14.54376 14.07316

H 27.11750 14.44801 14.41729

C 25.64946 15.71678 13.69135

H 26.05776 16.57494 13.71757

C 24.38320 15.45218 13.26856

H   23.76234   16.09647   12.95065

Table S4. 60 lowest TD-B3LYP excitation energies for gas-phase complex **1**

Root 1 singlet a   0.121008278 a.u.   3.2928 eV

Root 2 singlet a   0.130904121 a.u.   3.5621 eV

Root 3 singlet a   0.131349652 a.u.   3.5742 eV

Root 4 singlet a   0.134520921 a.u.   3.6605 eV

Root 5 singlet a   0.137581164 a.u.   3.7438 eV

Root 6 singlet a   0.138545074 a.u.   3.7700 eV

Root 7 singlet a   0.141372995 a.u.   3.8470 eV

Root 8 singlet a   0.142560493 a.u.   3.8793 eV

Root 9 singlet a   0.145724779 a.u.   3.9654 eV

Root 10 singlet a   0.149627556 a.u.   4.0716 eV

Root 11 singlet a   0.150410258 a.u.   4.0929 eV

Root 12 singlet a   0.154204751 a.u.   4.1961 eV

Root 13 singlet a   0.161097948 a.u.   4.3837 eV

Root 14 singlet a   0.162403951 a.u.   4.4192 eV

Root 15 singlet a   0.163608262 a.u.   4.4520 eV

Root 16 singlet a   0.164637703 a.u.   4.4800 eV

Root 17 singlet a   0.165965732 a.u.   4.5162 eV

Root 18 singlet a   0.167097585 a.u.   4.5470 eV

Root 19 singlet a   0.167704954 a.u.   4.5635 eV

Root 20 singlet a   0.168169165 a.u.   4.5761 eV

Root 21 singlet a   0.168804979 a.u.   4.5934 eV

Root 22 singlet a   0.169426325 a.u.   4.6103 eV

Root 23 singlet a	0.170068942 a.u.	4.6278 eV
Root 24 singlet a	0.171033772 a.u.	4.6541 eV
Root 25 singlet a	0.171386395 a.u.	4.6637 eV
Root 26 singlet a	0.172328313 a.u.	4.6893 eV
Root 27 singlet a	0.173034010 a.u.	4.7085 eV
Root 28 singlet a	0.175179974 a.u.	4.7669 eV
Root 29 singlet a	0.175713287 a.u.	4.7814 eV
Root 30 singlet a	0.175961249 a.u.	4.7882 eV
Root 31 singlet a	0.177421587 a.u.	4.8279 eV
Root 32 singlet a	0.177767896 a.u.	4.8373 eV
Root 33 singlet a	0.178258620 a.u.	4.8507 eV
Root 34 singlet a	0.179215071 a.u.	4.8767 eV
Root 35 singlet a	0.180216332 a.u.	4.9039 eV
Root 36 singlet a	0.181386030 a.u.	4.9358 eV
Root 37 singlet a	0.181999903 a.u.	4.9525 eV
Root 38 singlet a	0.182805998 a.u.	4.9744 eV
Root 39 singlet a	0.183480936 a.u.	4.9928 eV
Root 40 singlet a	0.184447578 a.u.	5.0191 eV
Root 41 singlet a	0.186310129 a.u.	5.0698 eV
Root 42 singlet a	0.186695466 a.u.	5.0802 eV
Root 43 singlet a	0.186879023 a.u.	5.0852 eV
Root 44 singlet a	0.187976412 a.u.	5.1151 eV
Root 45 singlet a	0.188805188 a.u.	5.1377 eV
Root 46 singlet a	0.189124246 a.u.	5.1463 eV
Root 47 singlet a	0.190526371 a.u.	5.1845 eV

Root 48 singlet a   0.190765036 a.u.   5.1910 eV

Root 49 singlet a   0.191206227 a.u.   5.2030 eV

Root 50 singlet a   0.191414593 a.u.   5.2087 eV

Root 51 singlet a   0.193275857 a.u.   5.2593 eV

Root 52 singlet a   0.193792226 a.u.   5.2734 eV

Root 53 singlet a   0.194362278 a.u.   5.2889 eV

Root 54 singlet a   0.195118377 a.u.   5.3094 eV

Root 55 singlet a   0.195283234 a.u.   5.3139 eV

Root 56 singlet a   0.196268137 a.u.   5.3407 eV

Root 57 singlet a   0.197292730 a.u.   5.3686 eV

Root 58 singlet a   0.197692159 a.u.   5.3795 eV

Root 59 singlet a   0.198522502 a.u.   5.4021 eV

Root 60 singlet a   0.199067401 a.u.   5.4169 eV

Table S5. Atomic positions (in angstrom) for a representative configuration of the hydrated form of **1**

Ru   -2.201   -17.906   14.064

C   -3.054   -19.498   12.702

C   -1.946   -16.076   13.067

C   -1.728   -19.175   12.407

P   -4.092   -17.011   14.962

P   -0.866   -17.040   15.670

C   -0.828   -19.496   13.341

C   -1.870   -19.978   14.541

C   -3.080   -20.019   13.973

H	-3.696	-19.395	12.120
N	-1.709	-15.151	12.564
H	-1.571	-18.792	11.561
C	-4.560	-15.288	14.899
C	-5.687	-17.659	14.433
C	-4.525	-17.218	16.753
C	-1.140	-15.328	16.361
C	0.927	-16.720	15.154
C	-0.426	-17.887	17.206
H	-0.080	-19.699	13.417
H	-1.497	-20.501	15.241
H	-3.825	-20.329	14.574
Ru	-1.124	-13.258	11.877
N	-5.886	-14.983	15.478
H	-4.413	-14.887	14.101
H	-3.988	-14.683	15.265
N	-7.006	-17.118	14.978
H	-5.682	-17.516	13.384
H	-5.810	-18.647	14.344
N	-5.859	-16.798	17.109
H	-4.452	-18.309	17.067
H	-3.932	-17.141	17.505
N	-0.082	-14.974	17.301
H	-1.234	-14.713	15.622
H	-1.922	-15.108	16.700

N	1.818	-16.108	16.364
H	0.756	-16.167	14.482
H	1.330	-17.425	14.708
N	0.492	-17.179	18.109
H	-1.321	-18.265	17.615
H	-0.086	-18.777	17.059
C	-2.396	-11.586	12.481
C	-1.288	-11.169	11.759
P	-2.278	-13.811	10.008
C	-0.138	-11.312	12.375
P	0.777	-14.222	11.158
C	-1.802	-12.063	13.654
C	-0.404	-11.929	13.597
C	-6.956	-15.726	14.723
C	-6.049	-15.395	16.885
C	-6.986	-17.458	16.432
C	1.333	-14.971	16.733
C	-0.049	-15.929	18.346
C	1.840	-17.034	17.463
H	-3.332	-11.274	12.400
H	-1.269	-10.590	10.886
C	-2.316	-12.774	8.560
C	-2.177	-15.388	9.148
C	-4.146	-13.914	10.298
H	0.692	-11.108	11.943

C	1.661	-13.704	9.652
C	2.293	-13.988	12.334
C	1.153	-15.944	10.955
H	-2.422	-12.484	14.181
H	0.078	-12.127	14.315
H	-7.835	-15.326	14.777
H	-7.118	-15.390	13.835
H	-5.397	-14.869	17.404
H	-6.750	-14.878	17.264
H	-7.797	-17.292	16.804
H	-6.986	-18.427	16.786
H	1.485	-14.141	16.148
H	1.937	-14.369	17.400
H	0.341	-15.513	19.241
H	-0.854	-16.079	18.880
H	2.315	-17.795	17.134
H	2.565	-17.015	18.074
H	-2.745	-11.764	8.926
N	-3.222	-13.166	7.461
H	-1.481	-12.369	8.269
N	-3.151	-15.592	8.004
H	-1.325	-15.754	8.868
H	-2.314	-16.180	9.795
H	-4.481	-13.182	10.711
N	-4.869	-14.253	8.981

H	-4.211	-14.608	10.921
N	2.966	-14.274	9.494
H	1.062	-13.589	8.811
H	1.700	-12.689	9.597
H	2.416	-13.058	12.644
N	3.629	-14.490	11.875
H	1.970	-14.284	13.239
H	0.556	-16.520	10.530
N	2.577	-16.357	10.704
H	0.717	-16.382	11.672
C	-2.878	-14.568	7.097
C	-4.669	-13.177	7.976
C	-4.505	-15.434	8.390
C	2.892	-15.651	9.492
C	3.883	-13.963	10.455
C	3.487	-15.927	11.687
H	-3.266	-14.889	6.149
H	-2.053	-14.431	6.655
H	-5.115	-13.130	7.136
H	-5.128	-12.418	8.312
H	-5.429	-15.600	7.872
H	-4.846	-16.243	8.792
H	3.719	-16.248	8.979
H	2.382	-16.126	8.775
H	4.877	-14.152	10.250

H	4.112	-12.936	10.473
H	3.387	-16.397	12.582
H	4.342	-16.323	11.638
O	-0.307	-7.566	13.389
H	-1.034	-8.035	13.704
H	0.335	-8.119	13.815
O	3.788	-12.784	16.284
H	4.261	-13.206	15.721
H	3.656	-12.199	17.048
O	2.298	-19.065	10.569
H	2.191	-18.081	10.509
H	2.685	-19.124	11.525
O	1.465	-8.452	15.261
H	2.057	-9.184	15.154
H	1.772	-7.759	15.791
O	-1.742	-10.835	17.425
H	-1.010	-11.258	17.687
H	-1.369	-9.877	17.475
O	-2.687	-8.820	14.317
H	-3.561	-8.984	14.006
H	-2.147	-9.821	14.360
O	-5.878	-11.153	14.710
H	-5.066	-10.600	14.643
H	-6.676	-10.616	14.522
O	-7.604	-14.650	9.867

H	-8.055	-14.036	9.358
H	-6.593	-14.407	9.755
O	1.971	-9.828	9.983
H	1.292	-10.186	9.264
H	1.873	-8.989	9.964
O	5.063	-13.075	13.585
H	4.355	-13.543	13.050
H	5.249	-12.336	12.978
O	-3.811	-10.261	7.617
H	-3.505	-11.164	7.483
H	-3.783	-9.857	6.835
O	4.045	-19.163	16.684
H	4.236	-18.268	16.058
H	4.864	-19.390	17.326
O	-4.263	-8.683	12.173
H	-4.202	-9.342	11.509
H	-5.034	-8.124	12.146
O	-5.297	-12.175	19.936
H	-4.776	-11.428	19.940
H	-5.533	-12.156	18.973
O	-4.732	-16.995	11.477
H	-5.603	-16.998	10.908
H	-4.209	-17.389	10.671
O	6.820	-16.479	13.086
H	6.498	-17.156	12.770

H	7.078	-16.211	12.156
O	-8.143	-13.705	12.445
H	-7.954	-14.370	11.583
H	-7.519	-12.900	12.194
O	0.098	-8.668	17.584
H	0.358	-8.461	16.612
H	0.697	-8.809	18.238
O	0.363	-12.277	18.215
H	0.266	-13.306	17.888
H	0.107	-12.566	19.118
O	1.659	-20.336	16.384
H	2.583	-19.966	16.585
H	1.564	-20.857	17.172
O	-5.678	-11.557	17.422
H	-5.887	-11.645	16.421
H	-5.510	-10.621	17.476
O	5.387	-17.908	11.189
H	4.753	-18.591	11.333
H	5.927	-18.135	10.474
O	0.489	-15.050	6.619
H	1.402	-15.475	6.484
H	-0.055	-15.702	6.960
O	-4.906	-10.572	10.044
H	-5.839	-10.830	9.869
H	-5.156	-9.983	9.313

O	3.520	-10.813	12.064
H	2.691	-10.588	11.614
H	4.078	-10.415	11.473
O	-0.858	-11.740	6.069
H	-1.646	-11.957	6.495
H	-0.644	-11.796	5.206
O	-5.981	-12.076	12.108
H	-5.665	-11.829	12.973
H	-5.240	-11.581	11.465
O	-2.780	-18.123	6.984
H	-1.942	-18.113	6.464
H	-2.826	-17.279	7.162
O	-0.258	-10.197	8.449
H	-0.525	-9.259	8.509
H	-0.504	-10.577	7.711
O	-4.317	-18.734	9.218
H	-4.888	-19.283	9.514
H	-4.205	-18.390	8.334
O	1.988	-12.250	6.713
H	1.005	-12.291	6.557
H	2.257	-13.218	6.813
O	2.784	-18.613	13.176
H	3.229	-17.959	13.834
H	2.426	-19.196	13.606
O	-0.213	-19.256	9.496

H	-0.886	-20.016	9.283
H	0.623	-19.500	9.849
O	0.001	-17.731	7.238
H	-0.156	-18.253	8.057
H	0.611	-18.267	6.849
O	-1.213	-14.635	4.741
H	-0.512	-14.809	5.487
H	-0.911	-14.996	4.032
O	-3.349	-12.773	16.553
H	-2.771	-12.014	16.834
H	-4.158	-12.395	16.868
O	-6.450	-17.588	19.671
H	-6.333	-16.700	19.970
H	-6.219	-17.347	18.713
O	4.284	-16.814	15.281
H	3.656	-16.152	15.579
H	5.186	-16.475	15.660

Table S6. 60 lowest TD-B3LYP excitation energies for a representative configuration of the hydrated form of **1**

Root 1 singlet a	0.113267651 a.u.	3.0822 eV
Root 2 singlet a	0.118036521 a.u.	3.2119 eV
Root 3 singlet a	0.120939319 a.u.	3.2909 eV
Root 4 singlet a	0.123612397 a.u.	3.3637 eV
Root 5 singlet a	0.124647148 a.u.	3.3918 eV
Root 6 singlet a	0.125745177 a.u.	3.4217 eV

Root 7 singlet a   0.128063698 a.u.   3.4848 eV

Root 8 singlet a   0.128584145 a.u.   3.4990 eV

Root 9 singlet a   0.129481984 a.u.   3.5234 eV

Root 10 singlet a   0.130409753 a.u.   3.5486 eV

Root 11 singlet a   0.131239164 a.u.   3.5712 eV

Root 12 singlet a   0.132634886 a.u.   3.6092 eV

Root 13 singlet a   0.134682884 a.u.   3.6649 eV

Root 14 singlet a   0.137189753 a.u.   3.7331 eV

Root 15 singlet a   0.137249982 a.u.   3.7348 eV

Root 16 singlet a   0.138320229 a.u.   3.7639 eV

Root 17 singlet a   0.139685616 a.u.   3.8010 eV

Root 18 singlet a   0.140246347 a.u.   3.8163 eV

Root 19 singlet a   0.140909353 a.u.   3.8343 eV

Root 20 singlet a   0.141359998 a.u.   3.8466 eV

Root 21 singlet a   0.143406915 a.u.   3.9023 eV

Root 22 singlet a   0.144182487 a.u.   3.9234 eV

Root 23 singlet a   0.144316696 a.u.   3.9271 eV

Root 24 singlet a   0.147679632 a.u.   4.0186 eV

Root 25 singlet a   0.149622117 a.u.   4.0714 eV

Root 26 singlet a   0.149781236 a.u.   4.0758 eV

Root 27 singlet a   0.150050277 a.u.   4.0831 eV

Root 28 singlet a   0.150897570 a.u.   4.1061 eV

Root 29 singlet a   0.151499408 a.u.   4.1225 eV

Root 30 singlet a   0.151718300 a.u.   4.1285 eV

Root 31 singlet a   0.152251330 a.u.   4.1430 eV

Root 32 singlet a	0.153187714 a.u.	4.1685 eV
Root 33 singlet a	0.153594095 a.u.	4.1795 eV
Root 34 singlet a	0.155254644 a.u.	4.2247 eV
Root 35 singlet a	0.155513237 a.u.	4.2317 eV
Root 36 singlet a	0.155832930 a.u.	4.2404 eV
Root 37 singlet a	0.156431407 a.u.	4.2567 eV
Root 38 singlet a	0.156509920 a.u.	4.2589 eV
Root 39 singlet a	0.158916527 a.u.	4.3243 eV
Root 40 singlet a	0.159285975 a.u.	4.3344 eV
Root 41 singlet a	0.159945521 a.u.	4.3523 eV
Root 42 singlet a	0.162049732 a.u.	4.4096 eV
Root 43 singlet a	0.162176393 a.u.	4.4130 eV
Root 44 singlet a	0.162877388 a.u.	4.4321 eV
Root 45 singlet a	0.164386241 a.u.	4.4732 eV
Root 46 singlet a	0.165261534 a.u.	4.4970 eV
Root 47 singlet a	0.167430187 a.u.	4.5560 eV
Root 48 singlet a	0.168042569 a.u.	4.5727 eV
Root 49 singlet a	0.168287891 a.u.	4.5793 eV
Root 50 singlet a	0.168549978 a.u.	4.5865 eV
Root 51 singlet a	0.168883441 a.u.	4.5956 eV
Root 52 singlet a	0.169413226 a.u.	4.6100 eV
Root 53 singlet a	0.169624092 a.u.	4.6157 eV
Root 54 singlet a	0.170150272 a.u.	4.6300 eV
Root 55 singlet a	0.171622959 a.u.	4.6701 eV
Root 56 singlet a	0.172083431 a.u.	4.6826 eV

Root 57 singlet a   0.173771098 a.u.   4.7286 eV

Root 58 singlet a   0.174261601 a.u.   4.7419 eV

Root 59 singlet a   0.174731012 a.u.   4.7547 eV

Root 60 singlet a   0.176305083 a.u.   4.7975 eV

[1] A. Romerosa, T. Campos-Malpartida, C. Lidrissi, M. Saoud, M. Serrano-Ruiz, M. Peruzzini, J. A. Garrido-Cardenas and F. Garcia-Maroto, *Inorg. Chem.*, 2006, **45**, 1289.

[2] (a) A. Altamore, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Moliterni, M.C.Burla, G. Polidori, M. Camalli and R. Spagna, *Sir 97 Package Program*, 1997; (b) G.M. Sheldrick, *SHELXTL Version 6.14; Bruker-AXS Madison, WI*, 2003.

[3] Experimental details of the X-ray crystal structure determination for complex **2** are given in the Supporting Information.

[4] Cambridge Structural Database (CDS): http://www.ccdc.cam.ac.uk/products/csd/ (October **2007**).

[5] (a) G. E. Pieslinger, P. Albores, L.D. Slep, B. J. Coe, C. J. Timpson and L. M. Baraldo, *Inorg Chem.,* 2013, **52**, 2906; (b) G. J. Baird, S. G. Davies, S. D. Moon, S. J. Simpson and R. H. Jones, *J. Chem. Soc. Dalton Trans.,* 1985, 1479.

[6] (a) A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza and M. Peruzzini, *Coord. Chem. Rev.*, 2004, **248**, 955; (b) D. N. Akbayeva, L. Gonsalvi, W. Oberhauser, M. Peruzzini, F. Vizza, P. Brüggeller, A. Romerosa, G. Sava and A. Bergamo, *Chem. Commun.,* 2003, 264; (c) A. Romerosa, T. Campos-Malpartida, C. Lidrissi, M. Saoud, M. Serrano-Ruiz, M. Peruzzini, J. A. Garrido-Cardenas and F. Garcia-Maroto, *Inorg. Chem.,* 2006, **45**, 1289; (d) C. A. Mebi and B. J. Frost, *Inorg. Chem.,* 2007, **46**, 7115; (e) S. Bolaño, J. Bravo, J. Castro, M. M. Rodríguez-Rocha, M. Fátima, C. Guedes da Silva, A. J. L. Pombeiro, L. Gonsalvi and M. Peruzzini, *Eur. J. Inorg. Chem.,* 2007, 5523; (f) A. Romerosa, M. Saoud, T. Campos-Malpartida, C. Lidrissi, M. Serrano-Ruiz, M. Peruzzini, J. A. Garrido and F. García-Maroto, *Eur. J. Inorg. Chem.,* 2007, 2803.

[7] (a) A. K. Soper, *RAL Tech. Rep.*, 2011, **RAL–TR–2011–012**; (b) A. K. Soper, *Mol. Simul.*, 2012, **38**, 1171; (c) H. Berendsen, J. Grigera, and T. Straatsma, *J. Phys. Chem.* **1987**, *91*, 6269.

[8] (a) A. Szabo and N. S. Ostlund, *Modern quantum chemistry*; Dover Publications Inc., Mineola, New York, 1996; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; (c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

[9] (a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; b) M. Valiev *at al.*, *Comput. Phys. Comm.*, 2010, **181**, 1477.