

Dalton Transactions

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: F. Scalambra, M. Serrano-Ruiz and A. Romerosa, *Dalton Trans.*, 2018, DOI: 10.1039/C7DT04515H.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Water driven formation of channels: unusual solid-state structural transformation of a heterometallic polymer

Franco Scalambra,^a Manuel Serrano-Ruiz^a and Antonio Romerosa*^aReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The backbone hetero-organometallic polymer *trans*-{[RuCp(PTA)₂-μ-CN-RuCp(PTA)₂-μ-CoCl₃]_n·(DMSO)_n (**1·DMSO**) has been synthesized and transformed into *cis*-{[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂-μ-CoCl₃]_n·[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂Cl]_{0.5n}·(15H₂O)_n (**2·15H₂O**) by the addition of water to the crystallization media (PTA = 1,3,5-triaza-7-phosphaadamantane). The new polymer **2·15H₂O** presents a nano-channeled molecular packing with pores filled by water molecules. The crystal structures of **1·DMSO** and **2·15H₂O** and the transformation process are herein presented and discussed.

Introduction, Results and discussion,
Experimental

New materials with interesting properties can be obtained incorporating metals in or among organic-polymeric frameworks.^{1,2} Transition metal centres can modify their oxidation states and/or facilitate the electron flow in ways impossible for organic materials,³ leading to new compounds with properties such as luminescence, extensive flame resistance, high flexibility, redox activity, etc.⁴ In 2005 we presented the first example of metal-backbone polymer containing an organometallic unit that was soluble in water.⁵ Few after the water soluble Ru-Ru-Au polymeric complex {[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂]-μ-Au(CN)₄]_n (PTA = 1,3,5-triaza-7-phosphaadamantane) was showed as the first example of a thermo-gel-hetero-organometallic polymer in water.⁶ After that we continued expanding the family of {[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂]-μ-MX_m]_n (M = transition metal, X = halide, pseudohalide) heterometallic complexes with new examples such as {[RuCp(PTA)₂-μ-CN-RuCp(PTA)₂]-μ-NiCl₃]_n⁷ and {[RuCp(PTA)₂-μ-CN-RuCp(PTA)₂]-μ-CdCl₃]_n,⁸ which were also water soluble and display particular properties both in water solution and solid state, as the formation of structured microparticles and the tendency to amorphize under mild conditions. These behaviours, joined with their crystallinity make of these polymers a new class of materials lying between metal organic frameworks (MOFs) and infinite coordination polymers (ICPs).⁹ After these initial findings other research teams explored the

use of PTA as a bidentate linker to obtain polymeric moieties with B, Zn, Cd, Hg and Ag, being the latter the most represented, giving polymers with interesting catalytic and bactericide behaviour.¹⁰

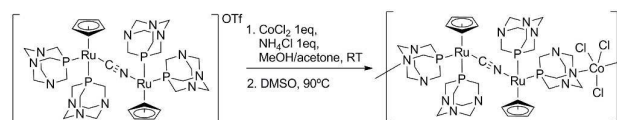
In this paper we present two new examples for the family of Ru-CN-Ru-M heterometallic polymers: the *trans*-{[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂]-μ-CoCl₃]_n·(DMSO)_n (**1·DMSO**) and the *cis*-{[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂]-μ-CoCl₃]_n·[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂Cl]_{0.5n}·(15H₂O)_n (**2·15H₂O**), which is a porous supramolecular system where water molecules are confined in nano-channels.

Results and Discussion

Complex **1·DMSO** was obtained by a robust and facile synthesis from a DMSO solution of the blue precipitate obtained by reaction of [RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂](CF₃SO₃)¹¹ with CoCl₂ in a mixture of MeOH/acetone (Scheme 1). The crystal structure of this heterometallic polymer is constituted by {-RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂-κN)-μ-CoCl₃-} repeating units (Scheme 1). A previous study on the reactivity of PTA against Co reports the oxidation of PTA during reaction, which has not happened in our case.¹² This polymer is similar to the previously published parent complexes *trans*-{[RuCp(PTA)₂-μ-CN-RuCp(PTA)₂]-μ-NiCl₃]_n·(2H₂O)_n·(4DMSO)_n (Ru-CN-Ru-Ni),⁷ and *trans*-{[RuCp(PTA)₂-μ-CN-RuCp(PTA)₂]-μ-CdCl₃]_n·(2DMSO)_n (Ru-CN-Ru-Cd).⁸ **1·DMSO** shows high stability even after months under air, as indicated by IR. The IR of **1·DMSO** shows a unique absorption band (2106 cm⁻¹) for the Ru-C≡N-Ru bridging ligand

^a Área de Química Inorgánica-CIESOL, Universidad de Almería, 04120, Almería (Spain). E-mail: romerosa@ual.es.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of **1**.

which lays at a slightly lower frequency than in the starting ruthenium dimer (2113 cm^{-1}) and higher than in the Ru-CN-Ru-Au polymer $trans\text{-}\{[\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2]\text{-}\mu\text{-Au}(\text{CN})_4\}_n$ (2097 cm^{-1}).⁶

The $^{31}\text{P}\{^1\text{H}\}$ NMR of **1**·DMSO in DMSO- d_6 shows a broad band at ca. 6 ppm similar to that found for the polymers Ru-CN-Ru-Au⁶ and Ru-CN-Ru-Ni,⁷ but different than the two singlets around -20 ppm found for $[\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2](\text{CF}_3\text{SO}_3)$.⁹ Evaporation of the solvent provided micro-crystals of **1**·DMSO. The polymer is slightly soluble in water ($S_{25^\circ\text{C}} = 12\text{ mg mL}^{-1}$), in which displays a $^{31}\text{P}\{^1\text{H}\}$ NMR spectra similar to those observed for polymers Ru-CN-Ru-Au⁶ and Ru-CN-Ru-Ni,⁷ and also for the dimer $[\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2](\text{CF}_3\text{SO}_3)$.⁹ Evaporation of the solvent leads to a blue powder whose IR spectrum is similar to that of **1**·DMSO but without the typical DMSO bands. The $^{31}\text{P}\{^1\text{H}\}$ NMR of this powder in DMSO- d_6 showed a broad band at ca. 6 ppm similar to that observed for the solution of **1**·DMSO. Evaporation of the solvent provided newly micro-crystals of **1**·DMSO. The ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1**·DMSO in D_2O and DMSO- d_6 were also found to be analogous to those of the $[\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2](\text{CF}_3\text{SO}_3)$ complex⁹ and polymers Ru-CN-Ru-Au⁶ and Ru-CN-Ru-Ni.⁷ Therefore, the NMR studies suggest that in water the polymer **1** is in equilibrium with the dimeric complex unit $\{\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2\}^+$. This fact was also confirmed by NMR diffusion studies in D_2O that showed that the hydrodynamic radius of the NMR active species in solution ($r_{(23^\circ\text{C}, \text{H}_2\text{O})} = 10.10\text{ \AA}$ and $r_{(23^\circ\text{C}, \text{DMSO})} = 8.80\text{ \AA}$) are similar to that found for the dimeric complex $\{\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2\}^+$ (9.09 \AA).¹⁴ The crystal structure of **1**·DMSO, which is discussed later, revealed that the Ru-CN-Ru-Co polymer is isostructural to the previously published Ru-CN-Ru-Ni⁷ and Ru-CN-Ru-Cd⁸ polymers, but with $\{\text{CoCl}_3\}$ units linking the dimeric Ru-CN-Ru moieties.

Given the results regarding the structure of the Ru-CN-Ru moiety in water obtained by neutron scattering studies in

combination with Empirical Potential Structure Refinement (EPSR) we decided to test the behaviour of **1**·DMSO in water. These studies showed that in water the dimeric ruthenium cationic complex $\{\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2\}^+$ strongly interacts with water molecules creating a stable hydrogen bond network around the complex.¹¹ The strong stability of the network could compensate the cleavage of a $\text{N}_{\text{PTA}}\text{-Co}$ bond, in principle stable, and promote the release of the Ru-CN-Ru units when **1** is in presence of enough water molecules. To obtain additional information on the influence of water in the $\text{N}_{\text{PTA}}\text{-Co}$ bond cleavage a battery of crystallizations in DMSO were performed in which the amount of water was carefully controlled. When a water/DMSO (1:10) mixture was used a new crystalline compound was obtained. It was observed that this conversion occurs also if **1**·DMSO is not previously dissolved in DMSO but just suspended. Crystals of **1**·DMSO were transformed into new ones in a water/DMSO mixture (1:10 in volume) without being apparently dissolved as showed by optical microscopy (Figure 1).

The obtained compound was characterized by single crystal X-ray diffraction as $cis\text{-}\{[\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2]\text{-}\mu\text{-CoCl}_3\}_n\cdot\{[\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2]\text{Cl}\}_{0.5n}\cdot(15\text{H}_2\text{O})_n$ (**2**·**15H₂O**), which is discussed later. When the ratio in volume of water/DMSO is larger than 1:10 the complex polymer **1**·DMSO partially converts into the new compound **2**·**15H₂O** but also other products form. These systems are currently under study to determine the mechanism of the process and the possible products that are formed.

Crystal structure of $trans\text{-}\{[\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2]\text{-}\mu\text{-CoCl}_3\}_n\cdot(\text{DMSO})_n$ (**1**·DMSO).

Single crystals of **1**·DMSO were obtained from a DMSO solution of the blue precipitate produced from the reaction of $[\text{RuCp}(\text{PTA})_2\text{-}\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2](\text{CF}_3\text{SO}_3)$ with CoCl_2 in a mixture of MeOH/acetone. Crystal data and bond lengths and angles are provided in Table S1-S3 in Supporting

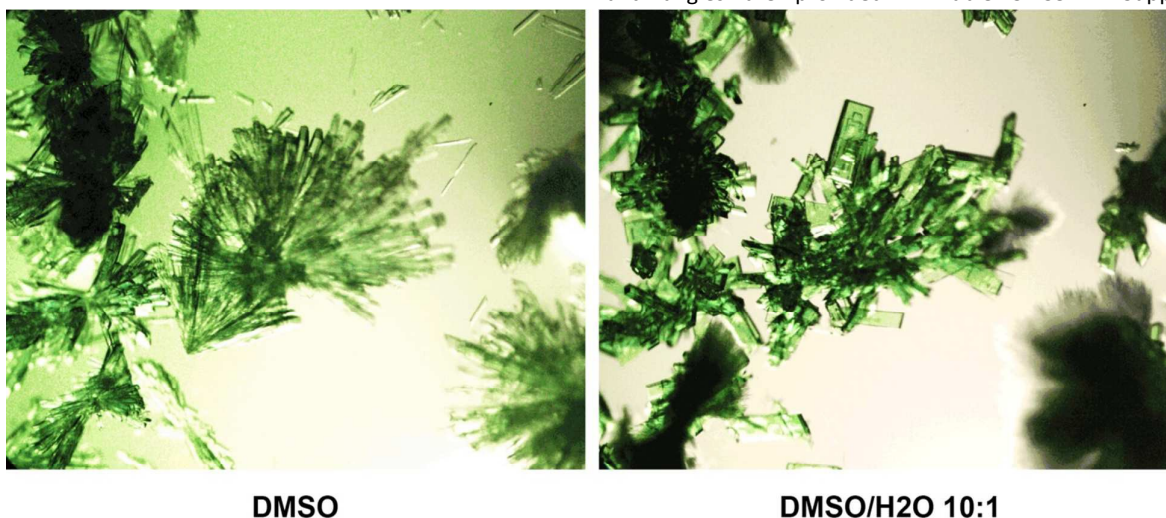


Figure 1. Picture of the crystals of **1**·DMSO (left) in DMSO and their transformation into **2**·**15H₂O** (right) upon the addition 10 % in volume of water.

Information. The cell asymmetric unit is constituted by a DMSO molecule and one dimeric $\{(-C/N-RuCp(PTA)(PTA)-\kappa N)-CoCl_2\}$ moiety, which is the basic repetition unit for the Ru-CN-Ru-Co heterometallic polymer **1** (Figure 2). The polymer is therefore constituted by binuclear Ru cationic complexes $\{RuClCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuClCp(PTA)_2\}^+$, in which two piano-stool $\{CpRu(PTA)_2\}$ moieties are linked by a CN⁻ ligand, and $\{CoCl_3\}^-$ moieties that are coordinated to the binuclear complexes by N_{PTA} atoms. As indicated, this polymer is similar to the previously published analog complexes $trans-\{[RuCp(PTA)_2-\mu-CN-RuCp(PTA)_2]_n-\mu-NiCl_3\}_n \cdot (2H_2O)_n \cdot (4DMSO)_n$,⁷ and $trans-\{[RuCp(PTA)_2-\mu-CN-RuCp(PTA)_2]_n-\mu-CdCl_3\}_n \cdot (2DMSO)_n$.⁸ The two $\{CpRu(PTA)_2\}$ units are disposed around the linking ligand CN⁻ in an opposite disposition as imposed by the symmetry inversion centre on the C≡N bond, which minimizes the repulsion among Cp and PTA ligands of both complex units. The C≡N bond lengths (Ru1-N1P(C1P) = 2.0292(19) Å; N1P≡C1P = 1.147(4) Å) are similar to those found for $\{RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2\}^+$ (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),¹⁴ the Ru-CN-Ru-Ni (Ru1-C2P(N2P) = 2.015(5) Å; Ru2-C1P(N1P) = 2.021(5) Å; N1P≡C1P = 1.141(10) Å; N2P≡C2P = 1.137(10) Å)⁷ and Ru-CN-Ru-Cd (Ru1-C1C(N1C) = 2.032(5) Å; Ru2-C1C(N1C) = 2.032(5) Å; (N1C)≡(C1C) = 1.158(7) Å).⁸ The Ru-CN-Ru bond lengths are similar to those found for Cp-ruthenium complexes containing coordinated CN⁻ and in $trans-\{[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2]_n-\mu-Au(CN)_4\}_n$ (Ru-CN-Ru-Au).^{6,13} The cobalt centre is constituted by a trigonal-bipyramidal Co(II) coordinated to three Cl in the meridian position and in the apical position to two N_{PTA} atoms from two different Ru-CN-Ru dimeric moieties. Similarly to the parent Ru-CN-Ru-Ni and Ru-CN-Ru-Cd metal polymers, the $\{CoCl_3\}^-$ units are coordinated through two PTA at opposite sides of the Ru-CN-Ru inversion centre, and therefore in *trans*-disposition (Figure 2). Both Co- N_{PTA} apical bond distances are crystallographically equivalent (Co2-N11 = 2.2831(17) Å) and

somewhat larger than those in Ru-CN-Ru-Ni (Ni1-N21 = 2.196(5) Å, Ni1-N51 = 2.221(4) Å)⁷ but significantly shorter than in Ru-CN-Ru-Cd (Cd1-N11 = 2.438(3) Å).⁸ In contrast with that obtained for the complexes Ru-CN-Ru-Ni and Ru-CN-Ru-Cd, in which two of the metal-chloride bond distance are similar but quite different to the third one (Ru-CN-Ru-Ni: Ni1-Cl1 = 2.3109(16) Å, Ni1-Cl2 = 2.3139(16) Å, Ni1-Cl3 = 2.3400(16) Å; Ru-CN-Ru-Cd: Cd1-Cl1 = 2.4692(12) Å, Cd1-Cl2 = 2.4727(9) Å), the three Co-Cl bonds in **1** are quite similar, being two of them crystallographically equivalent, (Co2-Cl1 = 2.3021(8) Å; Co2-Cl2, Co2-Cl2' = 2.3063(5) Å).

Despite of the similar Co-Cl bonds the tetragonal-bipyramidal coordination geometry around the metal is distorted (N11-Co2-N11 = 177.78(9)°, N11-Co2-Cl1 = 88.89(4)°, Cl1-Co2-Cl2 = 119.594(16)°) but not so decidedly as that in the Ni and Cd polymers (Ru-CN-Ru-Ni: N21-Ni1-N51 = 176.41(18)°, Cl2-Ni1-Cl3 = 107.62(6)°; Ru-CN-Ru-Cd: Cl1-Cd1-Cl2 = 119.15(2)°, Cl2-Cd1-Cl2 = 121.70(5)°, N1-Cd1-Cl1 = 88.61(7)°, N1-Cd1-N1 = 177.22(14)°). There are only two crystal structures of Co with a tetragonal-bipyramidal geometry in which metal is apically bonded to two nitrogens and to three chlorides in the meridian.¹³ The Co- N_{PTA} and Co-Cl bond lengths in **1** are similar to those for (1-aza-4-azoniabicyclo[2.2.2]octane- κN^2)(1,4-diazabicyclo[2.2.2]octane- κN^2)trichlorocobalt(II), (Co1-N1 = 2.269(3) Å, Co-Cl1 = 2.3080(8) Å),¹⁴ while are bigger than those for [Co(Hpiperazine)₂Cl₃](H₂O) (Co(1)-N(1) = 2.187(5) Å, Co(1)-N(3) = 2.203(5) Å, Co(1)-Cl(1) = 2.315(2) Å, Co(1)-Cl(2) = 2.325(2) Å).¹⁵ For what concern the C-N bonds of the bidentate PTA, their lengths are found between 1.487(3) and 1.494(3) Å, slightly longer than for the monodentate (1.464(3) – 1.472(3) Å). This fact agrees with the C-N elongation upon N-coordination in coordination compound containing bridging PTA ligands.¹⁶

The polymeric units pack together forming monolayers separated by DMSO molecules, being most of the interactions

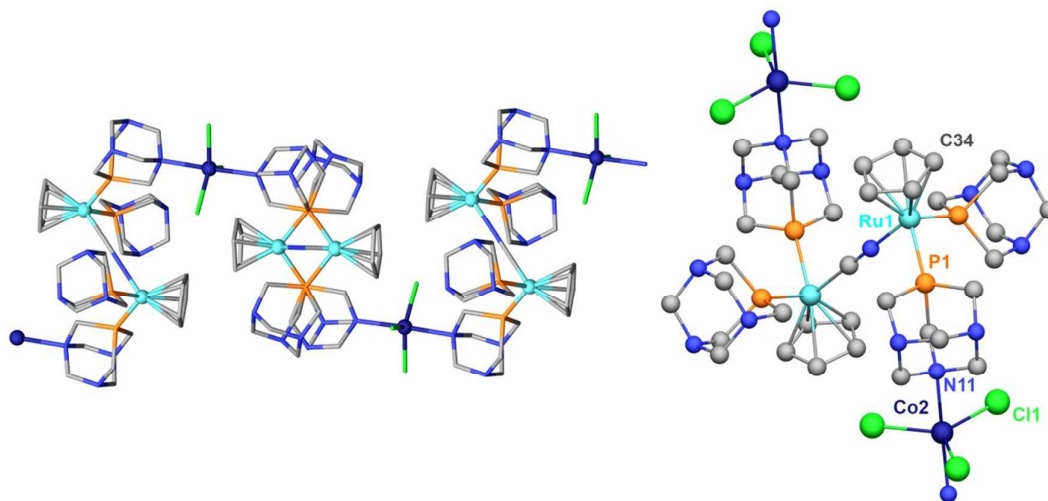


Figure 2. Left: of the *transoid* coordination of $\{CoCl_3\}^-$ moieties to the $\{RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2\}^+$ unit in the crystal of **1-DMSO**. Right: Ball and stick representation of the chain of **1** in the crystal structure hydrogen atoms were removed for clarity.

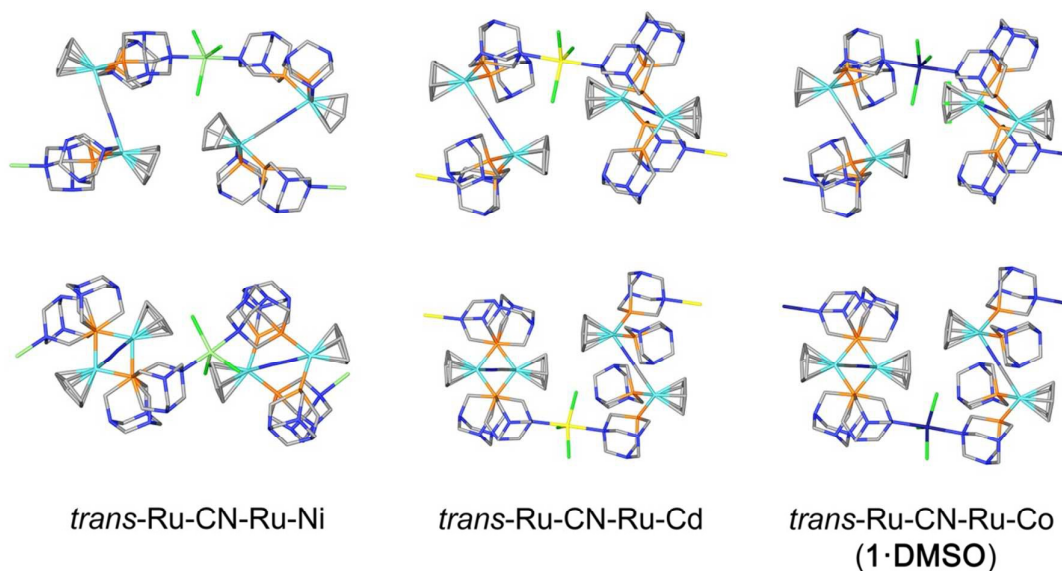


Figure 3. Comparative view of polymers *trans*-Ru-CN-Ru-Ni, *trans*-Ru-CN-Ru-Cd and *trans*-Ru-CN-Ru-Co (**1**·DMSO). The dihedral angle between consecutive Ru1-CN-Ru2 units are respectively: 32.8°, 102.2° and 104.3°.

between the non-hydrogen-polymer-layers and the DMSO molecules larger than 3 Å. Nevertheless there are interactions between DMSO-hydrogen atoms and **1** atoms somewhat shorter than van der Waals distances.

Crystal structure of *cis*-{[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂-μ-CoCl₃]}_n·{[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂]Cl_{0.5n}·(15H₂O)_n (2·15H₂O).

Complex **2**·15H₂O was obtained as single crystals from crystals of **1**·DMSO in a mixture of H₂O/DMSO (1:10). The cell asymmetric unit is constituted by one {[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂]-μ-CoCl₃} heterometallic moiety, which is the basic repetition unit of the heterometallic polymer, one [RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂]⁺, 0.5 Cl⁻ and 15 water

molecules. Therefore the compound **2** is constituted by a polymeric complex of formula {[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂]-μ-CoCl₃]_n, therefore similar in composition to **1** but, in contrast with it, the two {CoCl₃}⁻ units are bonded to N_{PTA} atoms of PTA ligands on the same side with respect to the Ru-CN-Ru dimer, in a *cis*-oid disposition (Figure 4).

Bond lengths and angles are provided in Tables S5-S6 in Supporting Information. The Ru-CN and Ru-NC bond lengths (Ru1-CCN1 = 2.020(5) Å; Ru2-NCN1 = 2.025(5) Å) are shorter than those found in **1** (Ru1-N1P(C1P) = 2.032(2) Å). The C≡N bond length is similar to that in **1** (**1**·DMSO: N1P≡C1P = 1.147(4) Å; **2**·15H₂O: CCN1≡NCN1 = 1.140(7) Å). The non-coordinated dimeric units {RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂}⁺, which act spacing the polymer chains of **2**, also contain a CN with C≡N bond length somewhat longer

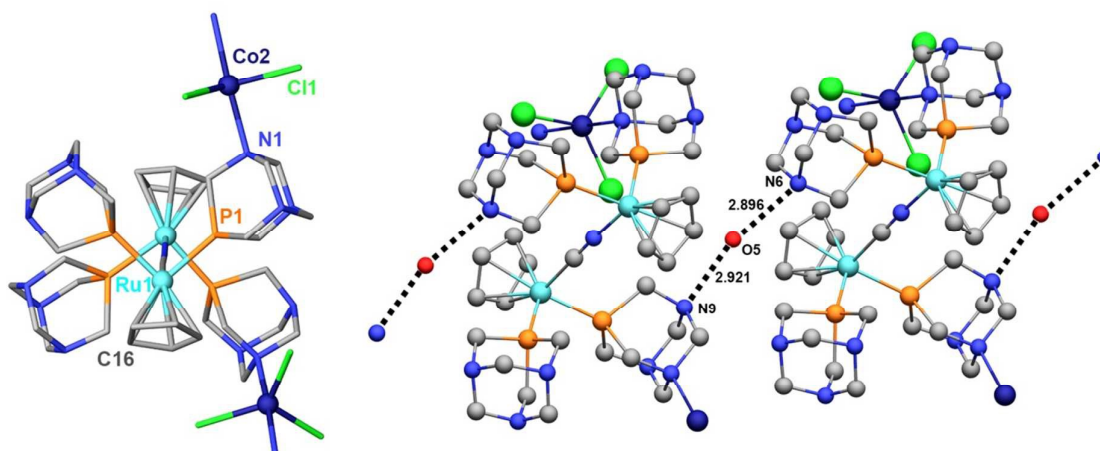


Figure 4. Left: ball and stick representation of *cis*-{[RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂]-μ-CoCl₃]_n in the crystal structure of **2**·15H₂O. Right: detail of the disposition of the Ru-CN-Ru-Co chains in layers by hydrogen bonds. Hydrogen atoms were eliminated for clarity.

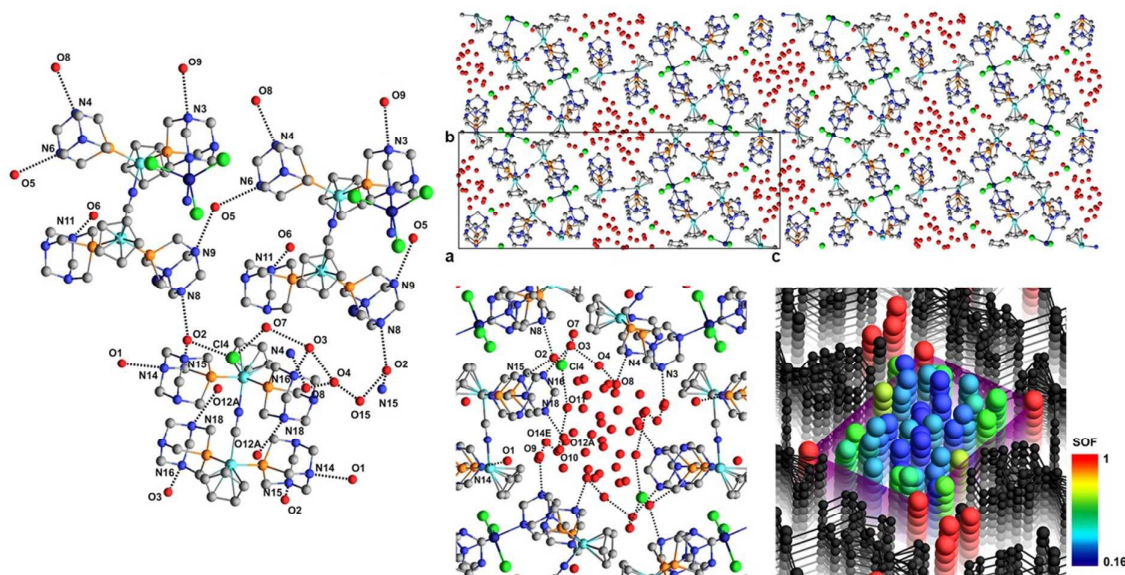


Figure 5. Left: hydrogen bond network involving Ru-CN-Ru dimers, Ru-CN-Ru-Co polymer chains and water molecules in the channels of **2·15H₂O**. Right: packing and site occupancy factors of the water molecules occupying the channels of **2·15H₂O**; the planes defining the channel are represented in purple. Hydrogen atoms were omitted for the sake of clarity.

(1.159(10) Å) and Ru-C(N) distance (2.013(5) Å) similar to those found in polymer **2**. The Co atoms connecting the dimeric Ru-CN-Ru units display a distorted trigonal-bipyramidal coordination sphere constituted by two apical N_{PTA} atoms and three Cl in the meridian plane (N1-Co1-N7 = 177.47(16)°; N1-Co1-Cl1 = 90.54(12)°; Cl1-Co1-Cl2 = 114.36(6)°; Cl2-Co1-Cl3 = 120.48(6)°), similarly to **1** (N11-Co2-N11 = 177.78(9)°, N11-Co2-Cl1 = 88.89(4)°, Cl1-Co2-Cl2(Cl2') = 119.594(16)°). Apical bond distances Co-N_{PTA} (Co1-N1 = 2.260(4) Å; Co1-N7 = 2.283(4) Å) and Co-Cl (Co1-Cl1 = 2.3220(14) Å; Co1-Cl2 = 2.3311(14) Å; Co1-Cl3 = 2.3433(14) Å) are similar to those in the trans-Ru-CN-Ru-Co polymer **1** (Co2-N11 = 2.2831(17) Å; Co2-Cl1 = 2.3021(8) Å; Co2-Cl2(Cl2') = 2.3063(5) Å). The elements present in the crystal of **2·15H₂O** are packed first in planes (Figure 4) by connection of *cis*-Ru-CN-Ru-Co polymer chains by strong hydrogen bonds through the N_{9PTA}, the water molecule O5 and N_{6PTA} (N9...O5...N6 = 2.921(6) Å, 2.896(7) Å). The spacing cations {RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂}⁺ are perpendicularly disposed to the layers (Figure 5), being connected each other by a strong hydrogen bond network. The packing of the *cis*-Ru-CN-Ru-Co polymers and dimeric Ru-CN-Ru cations generates parallel channels, which are extended along the crystal structure.

These channels, defined by the planes passing through the oxygen atoms O1 and O4 of consecutive unit cells, have respectively largest and shortest edge and diagonal lengths 9.25 Å, 7.20 Å, 13.826 Å and 9.162 Å. The water molecules that define the planes are in the vertices of a parallelepiped. Out of these borders six molecules of water and one chloride (distributed between two crystallographic positions) are found. Inside, 44 disordered positions were found, which contain 16 disordered oxygens of water molecules with occupancies in the range between 0.75 (O11) and 0.16 (O13A)

(Figure 5). An extended hydrogen bond network connects the water molecules among them, involving the Cl⁻, the Ru-CN-Ru dimers and Ru-CN-Ru-Co polymeric chains by their N_{PTA} (crystallographic hydrogen independent distances around the Ru-Ru dimer: Cl4...O2 = 2.803(8) Å, Cl4...O7 = 2.753(8) Å, O7...O3 = 2.817(8) Å, O3...O4 = 2.821(9) Å, O4...O15 = 2.69(1) Å, O2...O15 = 2.80(1) Å, N16...O3 = 2.871(7) Å, N15...O2 = 2.780(7) Å; 4...O8 = 2.70(2) Å, N4...O8 = 2.85(1) Å, N8...O2 = 2.817(6) Å). The water molecules O14B and O14D are separated from the nearest atoms by distances larger than those considered for hydrogen bonding.¹⁷ The water molecules outside the channel are strongly hydrogen bonded to each other, with the Cl⁻ and the polymer and dimer. In contrast, the disordered water molecules inside the channels are connected among them and with the outside water molecules by very weak hydrogen bonds.

The removal of the water in **2·15H₂O** has been studied by thermogravimetric analysis (Supplementary Information, Figure S21). The observed weight loss in the temperature range from 20° C to 140 °C, which is the characteristic temperature range for eliminating non-coordinated water molecules, was observed to be of 13.9 %. This weight lost is in good agreement with the elimination of 15 water molecules per asymmetric unit in **2·15H₂O** and therefore with the observed amount of water molecules in the crystal. It is interesting to stress that the water molecules are removed along a broad range of temperatures: from 23°C to and 80°C, which is significantly lower than the boiling point of water under atmospheric pressure.

Conclusions

The synthesis of backbone hetero-organometallic polymers containing $\{CpRu(PTA)_2-CN-1\kappa C:2\kappa^2 N-(PTA)_2RuCp\}^+$ and $\{CoCl_3\}^-$ have been found to be very sensitive to the amount of water present in the reaction. The *trans*- $[RuCp(PTA)_2-\mu-CN-RuCp(PTA)_2-\mu-CoCl_3]_n \cdot (DMSO)_n$ (**1-DMSO**), which is synthesized in absence of water, is transformed into *cis*- $\{[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2-\mu-CoCl_3]\}_n \cdot \{[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2]Cl\}_{0.5n} \cdot (15H_2O)_n$ (**2-15H₂O**) by the addition of water to the crystallization media. The water produces the partial cleavage of **1** giving rise to free $\{CpRu(PTA)_2-CN-(PTA)_2RuCp\}^+$ but also the isomerization from *trans*- $[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2-\mu-CoCl_3]$ to *cis*- $\{[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2-\mu-CoCl_3]\}_n$. These units are self-assembled around nano-channels containing water molecules and constitute the new compound **2-15H₂O**. Some of the water molecules are strongly bonded to the polymer by hydrogen bonds and some others are only weakly interacting with rest of water molecules. These interactions are so feeble that is possible to affirm that the water molecules are like in liquid state. This can be also noticed due to the relatively low temperature (23–80 °C) needed for their removal from inside the structure. The unexpected behaviour of fluid transport through nanoscale channels is an active focus of current research. The research about nanoconfined fluids is a fascinating interdisciplinary line of investigation with a large variety of possible applications such as sensors, desalination, catalysis, etc.¹⁸ There is a particular interest in carbon nanotubes from which such nanofluidic devices can readily be fabricated but also to understand the flow behaviour of water through biological pores. Carbon nanotubes with nanometre-scale diameters, for instance, support water flow rates that exceed the expectations of macroscopic hydrodynamics by orders of magnitude.¹⁹ The extraordinary transport properties of biological pores are due both to their specific and complex structures and to the unusual properties of fluids confined to such molecularly narrow pores, which are constituted by short peptides self-assembled. Biological nanopores are, hence, essential for all living cells but also offer fascinating possibilities for applications in nanobiotechnology.²⁰

To the best of our knowledge the transformation of **1-DMSO** into **2-15H₂O** is the first example of a water-driven self-assembly of a heterometallic polymer. Studies are in progress to determine the behaviour and properties of water molecules in **2-15H₂O** and to synthesize similar system with polymers containing other metals.

Experimental Section

General 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, the complexes $[RuClCp(PTA)_2]$ and $[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-$

$RuCp(PTA)_2](CF_3SO_3)$ and were prepared as described in the literature.^{10,21} 1H , $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and $^1H-^{13}C$ HSQC-DEPT NMR experiments were routinely conducted on the Bruker AV600 (600.13 MHz for 1H). Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (1H) or the deuterated solvent multiplet ($^{13}C\{^1H\}$). Chemical shifts for $^{31}P\{^1H\}$ NMR spectra were measured relative to external 85 % H_3PO_4 . Infrared spectra were recorded on KBr disks using a Bruker Vertex 70 FT-IR spectrometer. Elemental analyses (C, H, N, S) were performed on a Fisons Instrument EA 1108 elemental analyzer. TGA was run with a TGA Q50 (TA Instruments) setting a temperature ramp of 5 °C/min from 23 to 140 °C under a nitrogen flux of 50.0 ml/min.

Synthesis of *trans*- $\{[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2]-\mu-CoCl_3\}_n \cdot (DMSO)_n$ (**1-DMSO**).

Under vigorous stirring anhydrous $CoCl_2$ (114.3 mg, 0.88 mmol) and NH_4Cl (47.1 mg, 0.88 mmol) were solubilized in 10 mL of methanol and added to a solution of $[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2](CF_3SO_3)$ (1.00 g, 0.88 mmol) in 50 mL of acetone. The blue powder precipitated was decanted, washed with acetone (3 x 20 mL), Et_2O (3 x 10 mL) and dried under vacuum. The resulting powder was dissolved in 12 mL of DMSO at 70 °C and then let to cool down to room temperature. After 3 days light-blue crystals suitable for single crystal X-ray diffraction were obtained, which were filtered and dried under air. Yield: 574 mg (53%). IR (KBr): $\nu = 2108\text{ cm}^{-1}$ (CN). 1H NMR (300 MHz, D_2O , δ): 3.83 – 4.03 (m, 24H; NCH_2P), 4.42 – 4.55 (m, 24H; NCH_2N), 4.80 (s, 5H; $CpRuNC$), 4.95 (s, 5H; $CpRuNC$); $^{13}C\{^1H\}$ NMR (75 MHz, D_2O , δ): 55.15 (t, $^1J_{CP} = 8.77$ Hz; NCH_2P), 56.47 (t, $^1J_{CP} = 9.65$ Hz; NCH_2P), 70.78 (s; NCH_2N), 70.88 (s; NCH_2N), 77.62 (s; $CpRuNC$), 80.20 (s; $CpRuNC$), 152.02 (t, $^1J_{CP} = 22.88$ Hz; CN). $^{31}P\{^1H\}$ NMR (121 MHz, D_2O , δ): -20.0 (s, 1P; P-RuN), -22.6 (s, 1P; P-RuC); IR (cm^{-1})(KBr): $\nu = 2106$ (s; $\nu_{as}(\text{CN})$). Anal. calcd. for $C_{39}H_{70}Cl_3CoN_{13}O_2P_4Ru_2S_2$ (1308.50): C 35.80, H 5.39, N 13.92, S 2.60 %; found: C 34.32, H 5.86, N 11.82.

Synthesis of *cis*- $\{[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2]-\mu-CoCl_3\}_n \cdot \{[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2]Cl\}_{0.5n} \cdot (15H_2O)_n$ (**2-15H₂O**)

The product can be obtained through two different synthesis:

- The same synthesis of **1-DMSO** but, instead to filter the product, 1.2 mL of water have been added to the mother solution containing **1-DMSO**. After three days the obtained light green crystals were filtered and air-dried. Yield: 736.6 mg (43%).
- The dimeric complex $[RuCp(PTA)_2-\mu-CN-1\kappa C:2\kappa^2 N-RuCp(PTA)_2](CF_3SO_3)$ (50.0 mg, 0.040 mmol) was dissolved at 90 °C in 0.535 mL of a mixture of DMSO/ H_2O 10:1, the obtained solution was cooled and kept at 25 °C for 2 days. The light-green single crystals formed were filtered and dried under air. Yield: 39.1 mg (40%). 1H NMR (300 MHz, D_2O , δ): 3.83 – 4.02

(m, 24H; NCH₂P), 4.41 – 4.54 (m, 24H; NCH₂N), 4.80 (s, 5H; CpRuNC), 4.95 (s, 5H; CpRuCN); ¹³C{¹H} RMN (75 MHz, D₂O, δ): 55.14 (t, ¹J_{CP} = 8.86 Hz; NCH₂P), 56.47 (t, ¹J_{CP} = 9.79 Hz; NCH₂P), 70.77 (s; NCH₂N), 70.87 (s; NCH₂N), 77.63 (s; CpRuNC), 80.21 (s; CpRuCN), 152.01 (t, ¹J_{CP} = 21.00 Hz; CN). ³¹P{¹H} NMR (121 MHz, D₂O, δ): -20.0 (s, 1P; PRuN), -22.6 (s, 1P; PRuC); IR (cm⁻¹)(KBr): ν = 2114 (s; ν_{as}(CN)). Anal. calcd. for C₁₀₅H₂₃₄Cl₇Co₂N₃₉O₃₀P₁₂Ru₆ (3867.56): C 32.61, H 6.10, N 14.12 %; found: C 33.08, H 6.31, N 13.71 %.

Conversion of 1-DMSO into 2-15H₂O.

Into a biphasic system containing 600 μL of DMSO and crystals of **1-DMSO** (60 mg, 0.049 mmol) were added 60 μL of H₂O. After 24 h all the starting crystals were transformed into light-green crystals of **2-15H₂O**, as checked by single crystals X-ray diffraction. Complex **2-15H₂O** was also obtained when a 10% in volume of water was added to 10 of the DMSO dissolution of **1-DMSO**. Yield: 50.8 mg (52%).

Stability of 1-DMSO and 2-15H₂O in D₂O and DMSO-d₆.

Polymers **1-DMSO** (10 mg) and **2-15H₂O** (10 mg) were dissolved into 0.5 mL of D₂O and DMSO-d₆ in different 5 mm NMR tubes. Resulting solutions were studied by NMR at RT. The ¹H, ¹³C and ³¹P NMR of the solutions were similar to that for the complex {RuCp(PTA)₂-μ-CN-1κC:2κ²N-RuCp(PTA)₂}⁺ in the same conditions and remained stable for more than 4 days at room temperature. The polymers **1-DMSO** and **2-15H₂O** were obtained again as crystals from the studied solutions in DMSO-d₆ while from D₂O a similar blue powder was obtained from both NMR tubes. The obtained powders show a similar IR that is also similar to that for **1-DMSO** but without the typical DMSO bands. When this powders were dissolved in DMSO crystals of **1-DMSO** were obtained.

Single crystal X-ray diffraction.

The data collections of the two compounds 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 3.37° < 2θ < 53.46° for **1-DMSO** and 3.13 < 2θ < 52.04° for **2-15H₂O**. Empirical absorption correction was applied with T_{min} = 0.6564 and T_{max} = 0.7455 for **1-DMSO** and T_{min} = 0.709 and T_{max} = 0.746 for **2-15H₂O**. The structure was solved by direct methods with SIR2004 structure solution program and refined by full matrix least squares on F² (SHELXL 2018) using the Olex2 software.^{22,23,24} Anisotropic thermal factors were assigned to all the non-hydrogen and part of the oxygen atoms. All the H atoms were placed in calculated positions in both compounds and not refined. Diagrams were generated by using programs Olex2 and VMD.²⁵ **CCDC 1573950 (1-DMSO)** and **1572958 (2-15H₂O)** contain 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).

Crystal data for 1-DMSO.

Light-blue crystals of **1-DMSO** were obtained by slow evaporation of its DMSO solution. C_{38.5}H₇₀Cl₃CoN_{13.5}O₂P₄Ru₂S₂, Monoclinic, space group C2/c (no. 15), a = 18.4888(13) Å, b = 15.9993(12) Å, c = 17.5570(13) Å, α = 90.0, β = 96.1210(10), γ = 90.0, V = 5163.9(7) Å³, Z = 4, ρ_{calcd} = 1.683 g.cm⁻³, final R₁ value 0.0254 for 5452 independent reflections (I > 2σ(I)).

Crystal data for 2-15H₂O.

Light-green crystals of **2-15H₂O** were obtained from a H₂O/DMSO (1:10 in volume) solution of **1-DMSO**. C_{104.8}H₁₇₄Cl₇Co₂N_{39.2}O₃₄P₁₂Ru₆, Monoclinic, space group P2₁/c (no. 14), a = 11.7090(9) Å, b = 16.0946(12) Å, c = 44.352(3) Å, α = 90.0, β = 91.6510(10), γ = 90.0, V = 8354.8(11) Å³, Z = 2, ρ_{calcd} = 1.513 g.cm⁻³, final R₁ value 0.0599 for 16422 independent reflections (I > 2σ(I)). During the solution of the structure one chloride with haft occupancy was found that is in agreement with the properties of the complex. Nevertheless the location of the chloride was not evident during the solution of the structure due to the large number of water molecules. Taking in account that the chloride is an anion, it should be located in the structure fulfilling two conditions: a) it should be close to the cation and b) it should not be involved in hydrogen bonding with the N_{PTA}. The positions that satisfied this conditions and that led to a stable refinement are that assigned in the final structure to Cl4 (½ Cl), O4 (1 O) and O7 (1 O) (position "A" (O4): Xfrac, Yfrac, Zfrac = 0.3386(6), 0.4898(4), 0.10347(18); position "B" (O7): Xfrac, Yfrac, Zfrac = 0.9924(5), 0.3764(3), 0.15362(12); position "C" (Cl4): Xfrac, Yfrac, Zfrac = 0.8646(5), 0.3244(4), 0.10408(15)). To achieve this final assignment of the crystallographic positions the three atoms (Cl4, O4 and O7) were exchanged among the three positions but for the three possible combinations neither R factor nor the Goof varied. Thus we proceeded checking the respective untied Uiso and occupancy factor values and after refinement we discarded the assignment of ½ Cl to position C because it led to the highest Uiso when changed for 1 O (O Uiso = 0.082; 1/2Cl Uiso = 0.106). The variation of Uiso between the remaining two combinations (1 O in position C, ½Cl in position B) was comparable for both Cl4 and O7 but the untied occupancy factor of Cl4 fit better to 0.5 when assigned to position C (sof = 0.50 (position C) vs sof = 0.55 (position B)). Finally when riding hydrogens are set on the oxygen O7 in position B the R factor slightly decreases (from 5.99% to 5.96%) (For further details see Supporting Information).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

European Commission FEDER, Projects CTQ2015-67384-R (MINECO) and P09-FQM-5402 (Junta de Andalucía, PAI group FQM-317 and COST Action CM1302 (WG1, WG2). M. S.-R. thanks Excellence Project P09-FQM-5402 for a postdoctoral contract, F.S. to the U. of Almeria for a predoctoral grant.

Notes and references

- (a) P. Nguyen, P. Gómez-Elipse and I. Manners P., *Chem. Rev.*, 1999, **99**, 1515; A. S. Abd-El-Aziz, *Macromol. Rapid Commun.*, 2002, **23**, 995; (b) T. M. Swager and R. P. Kingsborough, *Progress in Organic Chemistry*, John Wiley & Sons, Inc., New York, 1999, **48**, 123; (c) I. Manners, *Synthetic Metal-Containing Polymers*, Wiley VHC, Verlag GmbH & Co. KGaA, 2004.
- F. S. Arimoto and A. C. Haven, *J. Am. Chem. Soc.*, 1955, **77**, 6295.
- G. R. Whittell, M. D. Hager, U. S. Schubert and I. Manners, *Nature Mater.*, 2011, **10**, 176.
- M. Serrano-Ruiz, F. Scalambra and A. Romerosa, *Advances in Organometallic Chemistry and Catalysis: The Silver / Gold Jubilee International Conference on Organometallic Chemistry Celebratory Book*, Wiley-VCH, Weinheim, 2014, 381.
- C. Lidrissi, A. Romerosa, M. Saoud, M. Serrano-Ruiz, L. Gonsalvi and M. Peruzzini, *Angew. Chem. Int. Ed.*, 2005, **44**, 2568.
- M. Serrano-Ruiz, A. Romerosa, B. Sierra-Martin and A. Fernandez-Barbero, *Angew. Chem. Int. Ed.*, 2008, **47**, 8665.
- F. Scalambra, M. Serrano-Ruiz and A. Romerosa, *Macromol. Rapid Commun.*, 2015, **36**, 689.
- F. Scalambra, M. Serrano-Ruiz, D. Gudat and A. Romerosa, *ChemistrySelect*, 2016, **5**, 901.
- A. M. Spokoyny, K. Dongwoo, S. Abdelqader and C. A. Mirkin, *Chem. Soc. Rev.*, 2009, **38**, 1218.
- (a) F. Mohr, L. R. Falvello and M. Laguna, *Eur. J. Inorg. Chem.*, 2006, **16**, 3152; (b) B. J. Frost, C. M. Bautista, R. Huang and Shearer, J., *Inorg. Chem.*, 2006, **45**, 3481; (c) A. M. Kirillov, A. M., S. W. Wiczorek, A. Lis, M. F. C. Guedes da Silva, M. Florek, J. Król, Z. Staroniewicz, P. Smoleński and A. J. L. Pombeiro, *Crystal Growth & Design*, 2011, **11**, 2711; (d) A. M. Kirillov, M. Filipowicz, M. F. C. Guedes da Silva, J. Kłak, P. Smoleński and A. J. L. Pombeiro, *Organometallics*, 2012, **31**, 7921.
- M. Serrano-Ruiz, S. Imberti, L. Bernasconi, N. Jadagayeva, F. Scalambra and A. Romerosa, *Chem. Commun.*, 2014, **50**, 11587.
- B. J. Frost, J. L. Harkreader and C. M. Bautista, *Inorg. Chem. Commun.*, **2008**, 580.
- Cambridge Structural Database (CDS): <http://www.ccdc.cam.ac.uk/products/csd/> (October 2017).
- R. G. Pritchard, M. Ali, A. Munim, and A. Uddin, *Acta Cryst.*, 2006, **C62**, m507.
- X. Zhao, M. Du, Y. Wang and X. H. Bua, *Journal of Molecular Structure*, 2004, **692**, 155.
- (a) B. J. Frost, W. C. Lee, K. Pal, T. H. Kim, D. VanDerveer and D. Rabinovich, *Polyhedron*, 2010, **29**, 2373; (b) S. W. Jaros, M. F. C. Guedes da Silva, J. Król, M. C. Oliveira, P. Smoleński, A. J. L. Pombeiro and A. M. Kirillov, *Inorg. Chem.*, 2016, **55**, 1486; (c) S. J. Zamisa and B. Omondi, *J. Coord. Chem.*, 2016, **69**, 3043; S. W. Jaros, M. F. C. Guedes da Silva, M. Florek, P. Smoleński, A. J. L. Pombeiro and A. M. Kirillov, *Inorg. Chem.*, 2016, **55**, 5886; (d) A. Lis, M. F. C. Guedes da Silva, A. M. Kirillov, P. Smoleński and A. J. L. Pombeiro, *Cryst. Growth Des.*, 2010, **10**, 5244; (e) S. W. Jaros, M. F. C. Guedes da Silva, M. Florek, P. Smoleński, A. J. L. Pombeiro and A. M. Kirillov, A. M.; *Cryst. Growth Des.*, 2014, **14**, 5408; (f) B. J. Frost, A. C. Mebi and P. W. Gingrich, *Eur. J. Inorg. Chem.*, 2006, **6**, 1182.
- F. Scalambra and A. Romerosa, *Non-covalent Interactions in the Synthesis and Design of New Compounds*, John Wiley & Sons, Inc.: Hoboken, NJ, 2015, 85.
- P. Sahu, S. M. Ali and K. T. Shenoy, *J. Chem. Phys.*, 2015, **143**, 184503.
- S. K. Bhatia, M. Rincon-Bonilla and D. Nicholsona, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15403.
- S. Majd, E. C. Yusko, Y. N. Billeh, M. X. Macrae, J. Yang and M. Mayer, *Current Opinion in Biotechnology*, 2010, **21**, 439.
- 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.
- M.C., Burla, R. Caliendo, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacobozzo, G. Polidori, D. Siliqi and R. Spagna, *J. Appl. Cryst.*, 2007, **40**, 609.
- (a) G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3; (b) G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
- O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.
- W. Humphrey, A. Dalke and K.; Schulten, *J. Mol. Graph.*, 1996, **14**, 33.

Water driven formation of channels: unusual solid-state structural transformation of a heterometallic polymer.

Franco Scalambra, Manuel Serrano-Ruiz, Antonio Romerosa*

Área de Química Inorgánica-CIESOL, Universidad de Almería, 04120, Almería (Spain)

E-mail: romerosa@ual.es

We describe the synthesis of an hetero-organometallic polymer, namely *trans*- $\{[(\text{PTA})_2\text{CpRu}-\mu\text{-CN-RuCp}(\text{PTA})_2-\mu\text{-CoCl}_3]\}_n \cdot (\text{DMSO})_n$, and its crystal-to-crystal transformation to its *cis* isomer upon addition of water to the crystallization medium. The change of conformation produces deep variations in its structure, as the formation of channels where water is nanoconfined.

