Experimental report

18/06/2024

Proposal: DIR-265 **Council:** 10/2022

Title: Determination of the water networkin a polymeric bimetallic Ru-Co compound.

Research area: Chemistry

This proposal is a new proposal

Main proposer: Antonio Manuel ROMEROSA-NIEVAS

Experimental team: Laura CANADILLAS DELGADO
Antonio Manuel ROMEROSA-NIEVAS
Franco SCALAMBRA

Local contacts: Laura CANADILLAS DELGADO

Samples: Ru-Co

Instrument	Requested days	Allocated days	From	To
D19	12	6	16/06/2023	22/06/2023

Abstract:

In the present proposal, we would like to study an organometallic-Ru-Co polymer (Ru-Co). Its single-crystal structure shows that distances among water molecules into the channels are larger than that expected for van der Waals interactions, which are easily eliminated by low vacuum. Neutron dispersion studies performed with TOSCA (at ISIS) revealed that probably the water molecules are confined by a new structure, possibly a pseudo-liquid or even could constitute an unknown ice phase (within the complex. This determination could show that water could exist in pseudo-liquid conditions at very low temperatures, like those found in external space, and could transport life throughout the cosmos. Despite water molecules constituting a new ice phase, this result is an interesting finding that will provide valuable information to know more about water and ice. We will intend to use D19 equipped with the 4-circle helium-based displex operated at 0.95 Å. This can reliably operate between temperatures of 2 K to room temperature (300 K), which facilitates determining the crystal structure of the complex Ru-Co but also the dynamic of water molecules into the channels at different temperatures.

Determination of the water network in the complex cis-{[{RuCp(PTA)$_2$-μ-CN-1κ*C*:2κ^2*N*-RuCp(PTA)$_2$}-μ-CoCl$_3$]}$_n$·{[RuCp(PTA)$_2$-μ-CN-1κ*C*:2κ^2*N*-RuCp(PTA)$_2$]Cl}$_{0.5n}$·(15H$_2$O)$_n$.

The incorporation of transition metals to polymeric moieties can give new species with mixed properties such as luminescence, flame resistance, high flexibility and redox responsivity. In this line, we have synthesized various examples of metal-backbone polymers incorporating the ligand PTA (PTA =1,3,5-triaza-7-phosphaadamantane) as a bidentate k^2*N*,*P*-linkerbetween {RuCp}$^+$ centres.[1-4] These compounds are generally hydrophilic, form structured microparticles in water and their crystals usually amorphize under very mild conditions, so that they can be considered as a new class of materials between metal-organic frameworks (MOFs) and infinite coordination polymers (ICPs).[5,6]

In the present proposal we would like to study the polymeric cis-{[{RuCp(PTA)$_2$-μ-CN-1κ*C*:2κ^2*N*-RuCp(PTA)$_2$}-μ-CoCl$_3$]}$_n$·{[RuCp(PTA)$_2$-μ-CN-1κ*C*:2κ^2*N*-RuCp(PTA)$_2$]Cl}$_{0.5n}$·(15H$_2$O)$_n$ (**Ru-Co**) compound. The single-crystal structure of this compound shows that distances among some of the water molecules contained in the channels are larger than that expected for van der Waals interactions. (see Figure 1).[7] These water molecules could be easily eliminated by low vacuum.

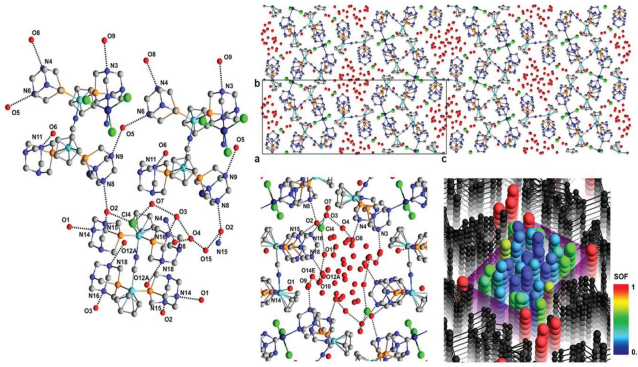

Figure 1. View detail (left) of the crystal structure and packing of complex **Ru-Co**.

Neutron dispersion studies performed with TOSCA (at ISIS) reveled that probably the water molecules are confined by a new structure, possibly a pseudo-liquid or even could constitute an unknown ice phase (within the complex channels) at 4 K. [8]

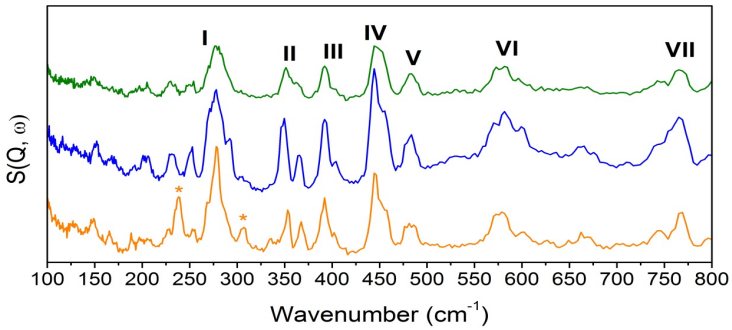

Figure 2. Region 100-800 cm^{-1} of the INS spectra of *trans*-[{RuCp(PTA)$_2$-μ-CN-1κ*C*:2κ^2*N*-RuCp(PTA)$_2$}-μ-CoCl$_3$]$_n$·(DMSO)$_n$ (**Ru-Co**-DMSO) (orange trace), **Ru-Co**

complex (blue trace) and {[{RuCp(PTA)$_2$-μ-CN-1κ*C*:2κ^2*N*-RuCp(PTA)$_2$}-μ-$CoCl_3$]}$_n$·{[RuCp(PTA)$_2$-μ-CN-1κ*C*:2κ^2*N*-RuCp(PTA)$_2$]Cl}$_{0.5n}$ (green trace). torsion band of CH_2 (I); the libration of the Cp (II, III); the CH_2-N(P)-CH_2 rocking (IV, V, VI) and CH_2-N(P)-CH_2 wagging (VII). DMSO-CH_3 torsions in **Ru-Co**-DMSO are denoted with (*).

Nevertheless a complete structural characterization by neutrons was not possible as not any enough large crystal was obtained until now.
We made a large number of attempts to obtain a single crystal of enough size to be determined by neutron diffraction and now we have a good crystal suitable for D19 measurements. This determination could show that water could exist in pseudo-liquid conditions at very low temperatures, like those found in external space, and could transport life throughout the cosmos.
Despite water molecules are constituting a new ice phase, this result is an interesting finding that will provide valuable information to know more about water and ice.

We can reproduce excellent quality single crystals of this compound with approximate size 2*2*3 mm, which are ideal for measurements at D19. Due to the potential of dehydration at room-temperature, crystals will be sent into the dissolution in which they were grown, conditions in which crystals are stable and retain water in the channels.
We will intend to use D19 equipped with the 4-circle helium-based displex operated at 0.95 Å. This can reliably operate between temperatures of 2 K to room temperature (300 K), which facilitate determine the crystal structure of the complex **Ru-Co** but also the dynamic of water molecules into the channels at different temperatures. Introducing the crystal into oil, previously to be mounting will avoid the loose of water because of the vacuum.

References:

[*1*]. C. Lidrissi, A. Romerosa, M. Saoud, M. Serrano-Ruiz, L. Gonsalvi, M. Peruzzini, Angew. Chem. Int. Ed. 2005, 44, 2568–2572; Angew. Chem. 2005, 117, 2624–2628.
[2] M. Serrano Ruiz, A. Romerosa, B. Sierra-Martin, A. Fernandez-Barbero, Angew. Chem. Int. Ed. 2008, 47, 8665–8669; Angew. Chem. 2008, 120, 8793–8797.
[3] F. Scalambra, M. Serrano-Ruiz, A. Romerosa, Macromol. Rapid Commun. 2015, 36, 689–693.
[4] F. Scalambra, M. Serrano-Ruiz, D. Gudat, A. Romerosa, ChemistrySelect 2016, 1, 901–905.
[5] A. M. Spokoyny, D. Kim, A. Sumrein, C. A. Mirkin, Chem. Soc. Rev. 2009, 38, 1218.
[6] B. Sierra-Martin, M. Serrano-Ruiz, V. García-Sakai, F. Scalambra, A. Romerosa, A. Fernandez-Barbero, Polymers (Basel) 2018, 10, 528.
[7]Franco Scalambra, Manuel Serrano-Ruiz and Antonio Romerosa, Dalton Trans. (2018), 47, 3588–3595.
[8]. Franco Scalambra, Svemir Rudić, and Antonio Romerosa, Eur. J. Inorg. Chem. (2019), 1155–1161.

Results

The crystal structure of cis-{[{RuCp(PTA)2-□-CN-1□C:2□2N-RuCp(PTA)2}-□-CoCl3]}n·{[RuCp(PTA)2-□-CN-1□C:2□2N-RuCp(PTA)2]Cl}0.5n·(15H2O)n (Ru-Co) determined by neutron diffraction (Figure) was found to be the same than that obtained by single crystal X-ray diffraction, which supports the presumption that no phase changes happen when temperature arrive to 2 K. Despite all attempts focused on improving the results by numerical methods that could improve the quality of the obtained results, the original data were not enough good to obtain results statistically good enough to support the results obtained by powder diffraction. Unfortunately, the size and quality of the crystals studied by neutron diffraction were not enough to obtain the excellent structural statistic that is required for determining whether water molecules are in movement into the channels of this complex at a so low temperature. A large number of crystallizations were targeted to obtain bigger quality crystals but all of them were unfruitful up to now. Nevertheless, the results obtained have been good enough to perform a theoretical study of this complex and support a request to study this complex by X-ray diffraction by synchrotron, measurements that will be performed in the next months. Also, the obtained results support going ahead in this research line both to study dipper this complex and synthesising similar compounds. We wish to publish or at least submit a paper including the obtained results before the end year.