

s13.m37.p3 **Crystallographic and Spectroscopic Studies of $[(n-C_4H_9)_4N]_3 NbW_5O_{19}$.** Mongi Debbabi¹, Hafdth Driss¹, Fatma Bannani¹, Ahmed Driss², ¹Laboratoire de Physico-chimie des Matériaux, Ecole Nationale d'Ingénieurs de Monastir, 5019 Monastir, Tunisie. ²Laboratoire de Crystallochimie, Faculté des Sciences de Tunis, 1004 Tunis, Tunisie. E-mail: mngdabb@enim.rnu.tn

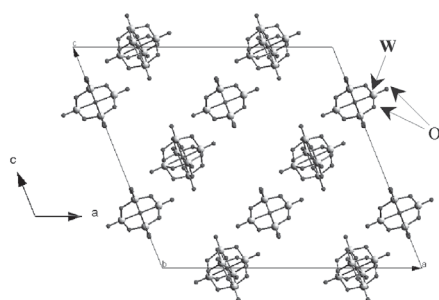
Keywords: Niobotungstates; Crystal structure; ¹⁸³W NMR

Hexaniobotungstates family ($Nb_nW_{6-n}O_{19}^{-2-n}$ $n=1,2,3,4$) [1] has not been, to date, characterized by crystallography, possibly due to complications arising from high charge, and large size, which are common difficulties in crystallization.

The compound $[(n-C_4H_9)_4N]_3 NbW_5O_{19}$ crystallizes in the monoclinic system, space group C2/c. The cell parameters are: $a=30.404 \text{ \AA}$, $b=18.595 \text{ \AA}$, $c=27.333 \text{ \AA}$, $\beta=112.455^\circ$, $V=14281.40 \text{ \AA}^3$ with $Z=8$. (-Fig 1-)

Final reliability factors are: $R=0.0405$ and $R_w=0.1036$ for 6412 reflections.

The structure of the compound $[NbW_5O_{19}]^{3-}$ is that of Lindqvist [2] which is close to O_h symmetry and which can be described as an assemblage of six polyhedron MO_6 ($M=W, Nb$) that are linked by shared edges.



-Fig 1-

The six metal positions are disordered and each site has some Nb and some W character with the following percentages in W: $M_1=85.907\%$ $M_2=82.737\%$ $M_3=80.917\%$ $M_4=84.751\%$ $M_5=82.112\%$ $M_6=83.735\%$.

In addition to X-ray crystallographic study, $[(n-C_4H_9)_4N]_3 NbW_5O_{19}$ was characterized by IR, Raman and multinuclear NMR (¹⁸³W, ¹⁷O).

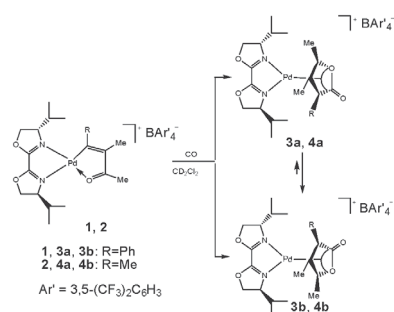
¹⁸³W chemical shifts show the two expected resonances with relative intensities 4:1 which emphasizes the C_{4v} local symmetry of the anion $[NbW_5O_{19}]^{3-}$.

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s13.m37.p4 **Combined Approaches to Characterize the Intermediates in Alkyne Cyclocarbonylations Promoted by Bioxazoline Pd(II) Complexes.** Annalisa Guerri^a, Carla Carfagna^b, Giuseppe Gatti^b, Luca Mosca^b and Paola Paoli^a, ^aDept. of Energy Engineering, University of Florence, Italy, and ^bInstitute of Chemical Science, University of Urbino, Italy. E-mail: a.guerri@ingfi1.ing.unifi.it

Keywords: Cyclocarbonylation reactions; Pd complexes; DFT calculations

Palladium catalyzed cyclocarbonylation of unsaturated compounds is a powerful methodology which allows direct preparation of cyclic compounds containing a carbonyl group in the ring, starting from readily available substrates [1]. Among these kinds of reactions, cyclocarbonylation of simple alkynes in the presence of palladium(II) species represents a well-established pathway for the synthesis of γ -lactones [2]. We have recently demonstrated, through isolation of the reaction intermediates (one of them fully characterized by X-ray diffraction), that the elementary steps involved in this process are the acylpalladation of an alkyne, followed by insertion of CO and cyclization to yield an α -diimine Pd complex in which the lactone moiety is coordinated in an η^3 -allyl fashion [3]. The aim of the present work is to study the products of the reactions of palladacycles **1** and **2** containing an optically active bioxazoline ligand with CO (scheme 1).



NMR and IR spectra revealed that, in each case, the reaction yields a mixture of two species in nearly equimolar ratio, each one characterized by an η^3 -allyl palladium structure containing a γ -lactone moiety. Particularly, each couple consists of two diastereoisomeric forms corresponding to the different coordinated face of the η^3 -allyl ligand. Leaving the mixture in solution, the conversion of one isomer into the other was observed, reaching a diastereoisomeric excess of more than 90%. The steric and electronic factors responsible for the epimerization process were investigated through molecular modeling, EHMO and DFT calculations on model compounds. The reliability of the optimized structures was checked by a comparison with the solid state structures of analogous complexes. The aim is to understand how the chiral ligand could produce asymmetric induction in the cyclocarbonylation process, and to use this knowledge for the catalytic synthesis of enantiomerically pure γ -butenolides.

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