

**o.m12.p13** Stereochemical study of natural sesquiterpenic complexes by X-rays. L. El Firdoussi, S. Allaoud, A. Karim. *Laboratoire de Chimie de Coordination- Faculté des Sciences Semlalia BP 2390, 40000 Marrakech-Maroc.*

Keywords: palladium, natural terpenes, organometallic.

Organic synthesis via ( $\pi$ -allyl) palladium complexes has attracted much attention in recent years. Pd(II) salts provide activation of the allylic position of an olefin, thus forming the basis for a variety of allylic alkylation reactions.

As part of our ongoing research for new catalytic materials it was of interest to prepare organometallic complexes based on natural terpenic alkenes. We describe here the synthesis and X-ray study of the ( $\pi$ -allyl) palladium complexes derived from natural sesquiterpenic himachalenes (essential component of *cedrus atlantica*). We have shown that this reaction occurs with high regio- and stereoselectivity by mixing  $\text{Na}_2\text{PdCl}_4$ ,  $\text{CuCl}_2$  and  $\text{NaOAc}$  in acetic acid medium (yield 54-60%). We have established the regiochemistry of the complexes by using high resolution NMR spectroscopy. However, depending on the coordination of the palladium on the  $\alpha$  or  $\beta$  faces of the ligands, two isomers could be obtained. In order to elucidate the stereochemistry of the final metal-free targets, it is essential to know the spatial structure of the complexes. We solve this problem by using X-ray diffraction of the complex which revealed unambiguously that the structures consist of dimeric units and the  $\text{Pd}_2\text{Cl}_2$  core is placed at the same face as the hydrogen in the cycle junction.

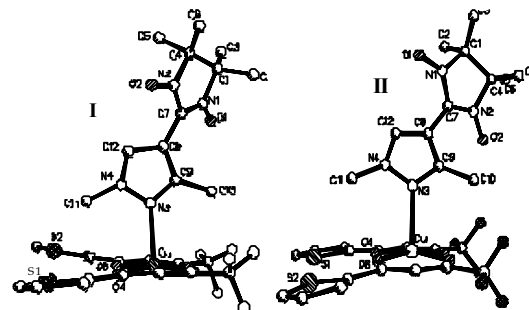
**o.m12.p14** Crystal structure of two modifications of  $\text{Cu}(\text{tta})_2$  complex with nitronylnitroxide. G. Romanenko<sup>1</sup>, I. El'tsov<sup>2</sup>, V. Ovcharenko<sup>2</sup>. <sup>1</sup>*Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia,* <sup>2</sup>*International Tomography Center SB RAS, Novosibirsk, Russia.*

Keywords: thenoyltrifluoroacetone, copper(II).

Crystal structures of two modification of  $\text{Cu}(\text{II})$  complex with thenoyltrifluoroacetone (tta) and nitronylnitroxide NITPz have been determined. Both crystal are triclinic with the space group  $P\bar{1}$  and  $Z=2$ . Unit cell parameters are  $a=10.129(2)$ ,  $b=13.381(1)$ ,  $c=13.658(5)$  Å,  $\alpha=75.29(1)$ ,  $\beta=75.70(2)$ ,  $\gamma=69.46(1)^\circ$ ,  $V=1651.0(7)$  Å<sup>3</sup>,  $d_c=1.523$  g/cm<sup>3</sup>,  $R_1=0.0795$  for I and  $a=8.016(6)$ ,  $b=10.962(7)$ ,  $c=19.680(9)$  Å,  $\alpha=105.00(3)$ ,  $\beta=97.92(4)$ ,  $\gamma=93.66(4)^\circ$ ,  $V=1645.5(18)$  Å<sup>3</sup>,  $d_c=1.528$  g/cm<sup>3</sup>,  $R_1=0.0869$  for II. The environment of Cu atoms established the square pyramid with four O atoms of two tta ligands in the base plane (Cu-O 1.921(3)-1.942(8) Å) and the N atom of pyrazole in apex. Cu-N distances are significantly different - 2.428(3) in I and 2.366(12) Å in II.

The distances in nitroxide groups of NITPz in I (1.281(6) and 1.275(6) Å) are slightly longer than that in II (1.268(15) and 1.255(15) Å). The differences in the molecular geometry of I and II are mostly remarkable in the values of torsion angles between different planes (table).

Atoms	Torsion angles, °	
	I	II
S1C17C16O4	-4.1	9.1
S2C25C24O6	7.2	-3.2
O4CuN3N4	29.6	57.9
O6CuN3N4	-58.9	-28.6
C12C7C7N2	-141.8	34.8
C12C7C7N1	39.0	-138.7



The molecules of  $\text{Cu}(\text{tta})_2\text{NITPz}$  are linked into dimers by weak  $\text{Cu}\cdots\text{S}$  contacts, which expand the copper environment up to 6. The differences in the molecular geometry produce the significant difference in intermolecular contacts:  $\text{Cu}\cdots\text{S}$  3.848 and 3.596 Å,  $\text{N1-O1}\cdots\text{O1}'-\text{N1}'$  4.372 and 3.454 Å,  $\text{N2-O2}\cdots\text{O1}'-\text{N1}'$  4.962 and 4.631 Å,  $\text{Cu}\cdots\text{Cu}$  5.547 and 6.805 Å for I and II consequently. These distinguishes are at the bottom of difference in the magnetic behavior of these modifications.