## METAL COMPLEXES

### Ruthenium/phosphine complexes: an effective tool to improve the cytotoxicity of natural product molecules

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Previous papers published by us have described the efficacy of ruthenium complexes with diimine, phosphine and picolinate ligands against cancer cells and *Mycobacterium tuberculosis*, where they showed strong *in vitro* and *in vivo* activity against tuberculosis, including multidrug-resistant bacteria [1, 2]. In the present work we have synthesized and characterized new ruthenium complexes containing phosphines, diimines and natural products as ligands, aiming to study their anticancer activities. The complexes showed to be more cytotoxic than the free ligands and the widely used anticancer drug cisplatin, under identical conditions. The cytotoxicity assays, *in vitro*, of the complexes against human tumor cell lines, including breast, prostate and lung, and against lung non-tumor human cell line, were carried out with the MTT method. In addition, we have analyzed the effect of ruthenium complexes on the mechanism of cell death. The complexes have ability to interact with CT-DNA and HSA and whether they cause cytotoxic effects in different tumor cell lines.

#### References

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## Cupric chloride complexes with 1-isopropyl-1*H*-1,2,4-triazole

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Cupric halide complexes with heterocyclic ligands show a great structural variety taking place due to the ability of  $Cu^{2+}$  cations to realize different types of coordination, and the ability of halide ions as well as heterocyclic ligands to form bridge linking. Realization of specific structural types of such complexes strongly depends on the nature and structure of heterocyclic ligands. To date, complexation of 1-*R*-1,2,4-triazoles with cupric halides has been investigated to

a small extent. Moreover, among complexes with the simplest 1-alkyl-1*H*-1,2,4-triazoles, only few complexes have been structurally characterized, namely with ethyl [1], butyl [2] and *tert*-butyl [3] substituted triazoles.

The present study is devoted to complexing behavior of 1-isopropyl-1H-1,2,4-triazole (L). This ligand was prepared in 80 % yield by the regioselective alkylation of 1,2,4-triazole with 2-propanol in sulfuric acid:

Triazole L was found to react with copper(II) chloride dihydrate to form complexes [CuL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>] (I) and [CuL<sub>4</sub>Cl<sub>2</sub>] (II). Both compounds were structurally characterized by single crystal X-ray analysis. It was found that complex I crystallizes in the monoclinic space group  $P 2_1/c$ , whereas complex II is triclinic (S. G.  $P\overline{1}$ ). Both compounds present mononuclear complexes, in which Cu<sup>2+</sup> cations lie on inversion centres (Fig. 1, 2).

 $Cu^{2+}$  cations adopt a distorted octahedral coordination in complexes I and II with coordination cores  $CuCl_2N_2O_2$  and  $CuCl_2N_4$ , respectively. In both compounds, ligands L are coordinated only *via* the triazole ring N<sup>4</sup> atoms. The coordination octahedrons in complexes I and II are considerably elongated at the expense of long axial bonds Cu–Cl, so the chlorine atoms can be considered as semi-coordinated. The bonds Cu–N and Cu–O are usual in the two complexes.

In the crystal structure of complex I, there are classic intermolecular hydrogen bonds  $O-H\cdots$ Cl of all water hydrogen atoms with chlorine atoms of neighboring complex molecules. These bonds are responsible for formation of hydrogen-bonded 2*D* network parallel to the *bc* plane. Complex II reveals only non-classic hydrogen bonds C-H···Cl between the triazole ring H and Cl atoms. Among them there are both intermolecular and intramolecular hydrogen bonds.



Fig. 1. Complex molecule of **I**, with the atom numbering for the asymmetric unit



Fig. 2. Complex molecule of **II**, with the atom numbering for the asymmetric unit

#### References

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# Dihydroxybenzoic acids as polydentate ligands in the organoantimony(V) complexes

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The determining factor of the product of the reaction between pentaphenylantimony (PPA) and dihydroxybenzoic acids is the location of functional groups in respect to each other in the benzene ring.

During the interaction of PPA with 2,5- and 2,6-dihydroxybenzoic acids the hydrogen atom is substituted only in the carboxyl group by the Ph<sub>4</sub>Sb fragment with obtaining compounds I and II, respectively (Fig.). The carboxyl group and *para*-hydroxyl group take part in the interaction between PPA and 2,4-dihydroxybenzoic acid. It leads to formation of the binuclear product III (Fig.). 2,3-Dihydroxybenzoic acid interacts with PPA like a diol without involving the carboxyl group with formation of the ionic complex IV (Fig.). The five-membered metallocycle is present in the complex's anion.