



## Short Lectures - Session A, Monday, June 11

SL - A1

### X-RAY SINGLE CRYSTAL STUDIES OF 10-ARYLFLAVINS

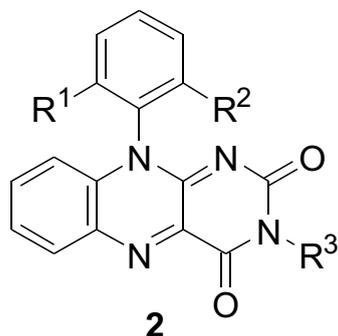
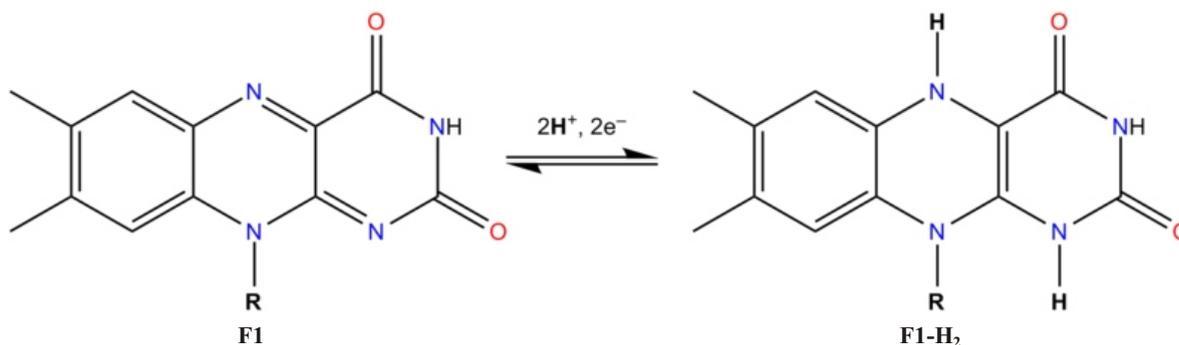
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**Flavins** (from Latin *flavus*, "yellow") are organic compounds based on pteridine, formed by the tricyclic heteronuclear organic ring - isoalloxazine. The biochemical source is riboflavin (also known as vitamin B2). Flavins are biologically active compounds which are responsible for redox processes in many types of enzymes, mostly in the form of flavin mononucleotide (FMN) or flavin adenin dinucleotide (FAD) co-factors [1]. Besides, synthetic flavin analogues are subject of intensive research as organocatalysts of oxidations and reductions [2, 3]. The flavin group is capable of undergoing oxidation-reduction reactions, and can accept either one electron in a two-step process or two electrons at once. Reduction is made with the addition of hydrogen atoms to specific nitrogen atoms on the isoalloxazine ring system:

are usually performed in the presence of air which allows regeneration of flavin catalyst (**FI**) from its dihydro form (**FI-H<sub>2</sub>**). Besides hydrogen bonding, flavins are known to interact with several molecules by p-p stacking, donor p interactions and cation- or anion- p interactions. These interactions were found to be essential not only for binding flavin cofactors but also for modulating redox properties and the reactivity of flavin moieties in the biological systems. However, intermolecular interactions can negatively influence the efficiency of flavin photocatalytic system decreasing the stability of flavins or doing their redox properties more unprofitable. With the aim to minimize a readiness of flavins to aggregate, we prepared series of derivatives with *ortho*-substituted phenyl ring in the position 10.



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
<b>a</b>	H	H	H
<b>b</b>	Me	Me	H
<b>c</b>	Et	Et	H
<b>d</b>	iPr	iPr	H
<b>e</b>	<i>tert</i> -Bu	H	H
<b>f</b>	Me	Me	Me

Until now, flavins have been applied for photooxidation of benzyl alcohols, benzyl amines or methylbenzenes to benzaldehydes, benzyl methyl ethers to methyl benzoates for photooxidation of dopamine, amino acids, indols, unsaturated lipids and fatty acids, glucose, fenols as well as for selective photocatalytic removal of benzylic protecting groups. The photooxidations mentioned above

Results of X-ray single crystal works of these derivatives will be presented.

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SL - A2

**EXPERIMENTAL ELECTRONIC STRUCTURE OF COORDINATION COMPOUNDS****Jozef Kožíšek, Peter Herich, Marek Fronc***Department of Physical Chemistry, Slovak Technical University, Bratislava, Slovakia  
josef.kozisek@stuba.sk***Introduction**

Properties of compounds are determined by their electronic structure. From the chemical point of view, the precise knowledge of the electronic structure of molecules is crucial to explain their possible reactivity, chemical and transport properties in various surroundings. Thus the experimental (such as ESR, voltammetry, electron spectroscopy, precise X-ray measurements) and theoretical (high-level quantum-chemical calculations) methods of the study of an exact electron density distribution in molecules are of increasing importance in recent studies in addition to common methods for determining their chemical structure (such as X-ray diffraction, NMR and vibrational spectroscopy, mass spectrometry).

Standard X-ray crystallography gives an information about the geometrical structure of the molecule under study. Over 500 000 crystal structures of organic and organometallic compounds in Cambridge Crystallographic Database have been solved using the software based on the spherical model of the atomic electron density. In the real compounds it is not adequate and the spherical part is only the 'core' of the atom. From the chemical point of view, the most interesting part of the electron density is the asymmetric one which reflects the changing electron density distribution

(EDD) due to the creation of chemical bonds. The EDD and its subsequent topological analysis is a powerful tool for the experimental study of the electronic structure (ES) of molecules in solid state [1].

**Experimental**

For study of experimental electron density distribution (EEDD) of some coordination compounds the GEMINI R data at 100K will be used. Theoretical study will be performed by a quantum-chemical software. The results of topological analysis both experimental and theoretical will be discussed [2-4].

*This work has been supported by Slovak Grant Agency APVV and VEGA (APVV-0202-10 and 1/0679/11).*

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SL - A3

**CHARGE DENSITY STUDY OF TETRAZOLE****L. Kucková, P. Herich, J. Kožíšek***Department of Physical Chemistry, Slovak University of Technology, 812 37 Bratislava, Slovakia  
lenka.kuckova@stuba.sk***Introduction**

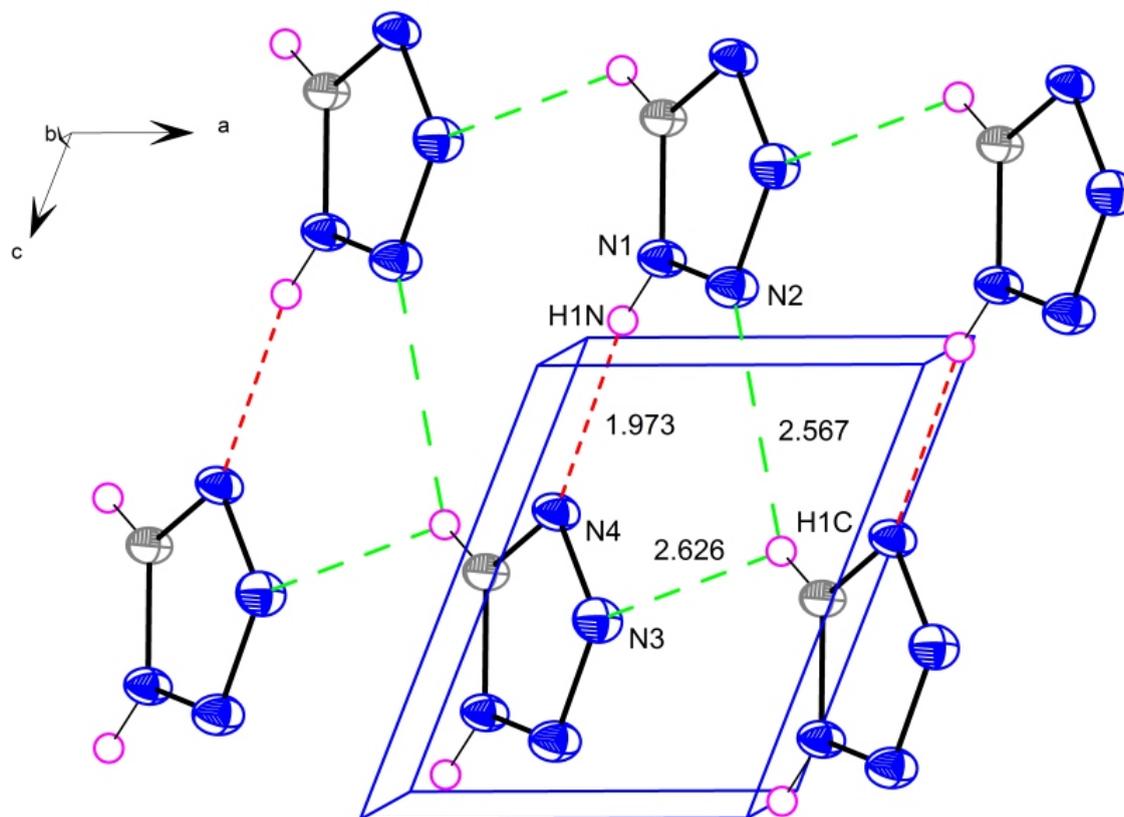
Comparison of experimental and theoretical electronic structure is very important. In many cases the number of atoms of the studied system make difficulties. In this work tetrazole was carefully chosen as the smallest single molecule in the unit cell. This work deals with the study of experimental electronic structure of tetrazole.

Tetrazole and its derivatives have attracted considerable attention because of their characterful structure and their applications as anti-allergic, antihypertensive, antibiotic and anticonvulsant agents. Therefore it plays an important role in medicinal chemistry. Tetrazoles, as quite suitable ligands, can serve as replacement for carboxylic acid also in supramolecular chemistry. Moreover, tetrazoles are highly flexible ligands and can easily adapt to different binding modes [1-5].

**Experimental**

Tetrazole was purchased from Sigma Aldrich as a solution for reaction. After the solvent was vaporized, the crystals were prepared by slow crystallization from the mixture of ethanol – isobutanol (6:1).

A single crystal of tetrazole was selected and mounted in the cold nitrogen stream. The data were collected at 100.0 (1) K on an Oxford Diffraction Kappa geometry GEMINI R diffractometer equipped with Ruby CCD area detector using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 50 kV and 40 mA. Distance from crystal to detector was 53 mm. Details of the X-ray diffraction experiment conditions and the crystallographic data for tetrazole are given in Tab. 1. Crystal structure was solved and refined by using SHELXS-97 and SHELXL-97. The



**Figure 1.** A perspective view of tetrazole (ellipsoids are drawn in 50 % probability factor). Contact distances and hydrogen bonds are shown by dotted lines.

molecular structure of tetrazole and its perspective view are shown in Fig. 1.

Starting parameters for multiple refinement were taken from a routine SHELXL refinement and all other refinements were carried out on F using the XD suite of programs [6]. A complete atom-centered multipole refinement was

carried out with the nonspherical atomic electron density given by the equation (1) [7].

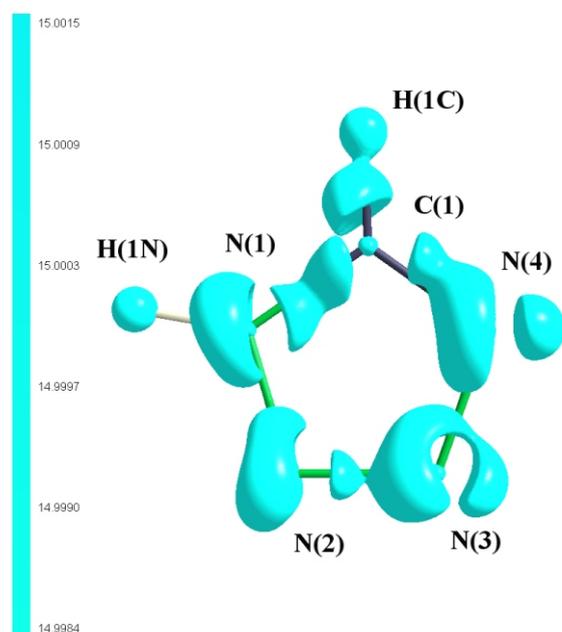
$$\rho_{at}(r) = \sum_{l=0}^{l_{\max}} \frac{P_c}{l+1} \rho_{core}(r) + \sum_{l=0}^{l_{\max}} \frac{P_v}{m+1} \rho_{valence}(r) + \sum_{l=1}^{l_{\max}} \sum_{m=0}^l \frac{P_{lm}}{d_{lm}} Y_{lm}(\theta, \phi) \quad (1)$$

**Table 1.** Crystal data and experimental details for tetrazole.

Empirical formula	C H <sub>2</sub> N <sub>4</sub>	Crystal size	0.264 0.162 0.058 mm
Formula weight	70.07	range for data collection	4.68° to 45.59°
Temperature, wavelength	293 (2) K, 0.71073 Å	Index ranges	-7 ≤ h ≤ 6
Crystal system, space group	triclinic, P 1		-9 ≤ k ≤ 9
Unit cell dimensions	a = 3.6064 (4) Å		-9 ≤ l ≤ 9
	b = 4.7373 (6) Å	Max. and min. transmission	0.994 and 0.977
	c = 4.9287 (9) Å	Reflections collected	5398
	α = 107.1 (1)°	Independent reflections	1961 (R(int) = 0.0333)
		Completeness to 2	100 %
		Data / restraints / parameters	1961 / 3 / 46
Formula units per unit cell	1	Goodness-of-fit on F <sup>2</sup>	1.041
Calculated density	1.589 mg m <sup>-3</sup>	Final R indices [I > I]	R1 = 0.0388, wR2 = 0.0984
Absorption coefficient	0.124 mm <sup>-1</sup>	R indices (all data)	R1 = 0.0434, wR2 = 0.1034
F (000)	36	Largest diff. peak and hole 0.349 and -0.404 (eÅ <sup>-3</sup> )	0.349 and -0.404 (eÅ <sup>-3</sup> )

**Table 2.** Summary of the SHELXL and multipole refinement of tetrazole.

	SHELXL refinement	Multipole refinement
$R(F)$	-	0.0188
$R(F)^\dagger$	-	0.0191
$wR(F)^\dagger$	-	0.0148
$R(F^2)$	0.0388	0.0241
$R(F^2)^\dagger$	0.0434	0.0242
$wR(F^2)^\dagger$	0.1034	0.0300
$S$	1.041	1.4455


**Figure 2.** 3D plots of the Laplacian of the electron density in tetrazole.

The H atoms were treated with one bond-directed dipole ( $l = 1$ ), other atoms were refined up to octapoles. The local coordinate systems to define multipoles were used as follows. For non-hydrogen atoms:  $x$ -axis - direction to the closest atom,  $y$ -axis - perpendicular to the  $x$ -axis and oriented towards the second closest atom; for hydrogen atoms:  $z$ -axis - direction to the bonding carbon or nitrogen

atom and  $x$ -axis - perpendicular to the  $z$ -axis. The strategy for refinement was as described previously [6]. The results of refinement are summarized in Tab. 2.

As can be seen in Table 2, the multipole refinement resulted in a significant improvement of the agreement between the experimental and calculated structure factors. Residual density maps were calculated by a Fourier synthesis where the coefficients are differences between the observed and calculated structure factors corresponding to the converged multipole model.

The maximum and minimum of the residual density are  $+0.108 \text{ e}/\text{\AA}^3$  and  $-0.074 \text{ e}/\text{\AA}^3$ , respectively; the root-mean-square residual density is  $0.034 \text{ e}/\text{\AA}^3$ . Atoms in ring are bonded by covalent bonds. Inspection of the maximum charge concentrations in the bonding and nonbonding regions in the valence shell, the so-called valence shell charge concentrations (VSCCs) shows that there are three charge concentrations (Fig. 2), which correspond to lone electron pairs on nitrogen atoms. On the other hand, the depletion of the charge in the regions where the covalent bonds are formed by interaction with the lone pair on carbon and nitrogen donor atoms (C(1), N(1), N(2), N(3) and N(4)) is clearly seen (Fig. 2).

### Acknowledgements

This work has been supported by Slovak Grant Agency APVV (APVV-0202-10) and VEGA (1/0679/11).

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SL - A4

## SYNTHESIS OF NEW DITHIOLATE COMPLEXES OF TRANSITION METALS

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Coordination compounds of transition metals in the oxidation state M(III) are quite unusual. The series of several dithiolate complexes of general formula R[M(bdt)<sub>2</sub>] with benzene-1,2-dithiol (bdt), M = Ni, Co and Cu as the central atom and various ammonium (phosphonium) derivatives R = Me<sub>4</sub>N<sup>+</sup>, Et<sub>4</sub>N<sup>+</sup>, Pr<sub>4</sub>N<sup>+</sup>, Me<sub>3</sub>PhN<sup>+</sup>, MePh<sub>3</sub>P<sup>+</sup>, Ph<sub>4</sub>P<sup>+</sup>, were prepared [1]. A wide range of technical applications (e.g. superconductors, resins, polarization filters, vulcanization accelerators) of the dithiolate complexes, as well as their biological activity (anticholinesterase activity, pesticides) makes them interesting subjects for the research. Our previous attempt to study the electronic structure of these complexes from diffraction data was not successful due to large anisotropic displacement parameters (ADPs) [2]. In order to reduce the thermal motion in the complex, chloro-substituted ligand, 3,6-dichloro-1,2-benzenedithiol (bdtCl<sub>2</sub>) was used for the synthesis.

Preparation of (Me(Ph)<sub>3</sub>P)[Cu(bdtCl<sub>2</sub>)<sub>2</sub>]: Solution of Na (0.08 g, 3.3 mmol) in MeOH (10 cm<sup>3</sup>) was added to 3,6-dichloro-1,2-benzenedithiol (bdtCl<sub>2</sub>, 95%) (0.34 g, 1.6 mmol). To this mixture, CuCl<sub>2</sub>·2H<sub>2</sub>O (98%) (0.13 g, 0.76 mmol) in MeOH (10 cm<sup>3</sup>) was added. Finally, Methyltriphenylphosphonium bromide (Me(Ph)<sub>3</sub>PBr, 99%) (0.57 g, 1.6 mmol) in MeOH (10 cm<sup>3</sup>) was added. The resulting solution was stirred for 24 hours. The complex was precipitated by the slow addition of water, with vigorous stirring. The green crystalline powder was filtered off, washed with diethyl ether, and then recrystallized from acetone/methanol solution (40:5) (yield 99%). Crude product was purified by column chromatography using eluent mixture toluene/methanol (10:1). The same procedure was used for preparation of complexes (Me(Ph)<sub>3</sub>P)[Ni(bdtCl<sub>2</sub>)<sub>2</sub>]; NiCl<sub>2</sub>·6H<sub>2</sub>O (98%) (0.18 g, 0.76 mmol) and (Me(Ph)<sub>3</sub>P)[Co(bdtCl<sub>2</sub>)<sub>2</sub>]; CoCl<sub>2</sub>·6H<sub>2</sub>O (98%) (0.18 g, 0.76 mmol). After crystallization a single crystal suitable for X-ray analysis was selected. All solvents were products of LACHEMA Brno and mikroCHEM. The chemicals of analytical grade were purchased from Sigma-Aldrich.

X-ray data collection for (Me(Ph)<sub>3</sub>P)[Cu(bdtCl<sub>2</sub>)<sub>2</sub>]; (Me(Ph)<sub>3</sub>P)[Ni(bdtCl<sub>2</sub>)<sub>2</sub>] and (Me(Ph)<sub>3</sub>P)[Co(bdtCl<sub>2</sub>)<sub>2</sub>] were performed on an Oxford Diffraction Gemini R four circle k-axis diffractometer equipped with a Ruby CCD detector and a graphite monochromator, using Mo-K radiation at 293(2) K and 100(2) K. CrysAlis program package (Oxford Diffraction, 2011) was used for data reduction [3]. The structure was solved by direct methods using SHELX [4, 5] and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares. All hydrogen atoms were found from the Fourier map and were refined isotropically. DIAMOND was used for drawing [6].

The three prepared complexes are found to be isostructural, crystallizing in the space group P21/c. The structures consist of two complex anions and one molecular cation. The central atom is coordinated by two dithiolates ligands. The X-ray structure analysis of (MePPh<sub>3</sub>)[Ni(bdtCl<sub>2</sub>)<sub>2</sub>], (MePPh<sub>3</sub>)[Co(bdtCl<sub>2</sub>)<sub>2</sub>] and (MePPh<sub>3</sub>)[Cu(bdtCl<sub>2</sub>)<sub>2</sub>] confirmed a square-planar geometry of S<sub>2</sub>MS<sub>2</sub> chromophore. The M-S bond lengths are for Ni: 2.1390(6)-2.1508(6) Å, for Co: 2.1570(6)-2.1640(6) Å and for Cu: 2.1720(6)-2.1761(5) Å, which are significantly shorter than the usual published values for metal(II) complexes (Ni: 2.17-2.18 Å [7], Co: 2.28 Å [8] and Cu: 2.27 Å [9]); this fact also supports the assumption of a metal(III) oxidation state in these compounds. The appropriate bond angles around central atoms (Ch1, Ch2°)-(Ch1, Ch2°) are (87.33(2), 87.74(2)°)-(92.67(2), 92.26(2)°) for NiS<sub>4</sub>, (87.66(2), 88.14(2)°)-(92.34(2), 91.86(2)°) for CoS<sub>4</sub> and (87.10(2), 87.57(2)°)-(92.90(2), 92.43(2)°) for CuS<sub>4</sub> chromophore. The structures of these complexes are stabilized by interaction of H27A-C11 (dist.: 2.905 Å) for Ni complex, (dist.: 2.896 Å) for Co complex and (dist.: 2.912 Å) for Cu complex. The basic idea of this work was to obtain suitable M(III) compounds for study of electronic structure. The chloro-substituted ligand was used to eliminate disorder (Figure 1). The elimination of disorder was successful. After purification the high quality crystals were prepared for the study of electronic structures.

This work has been supported by Slovak Grant Agency APVV (APVV-0202-10) and VEGA (1/0679/11).

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extended abstract submitted