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Copper complexes as biomimetic models of catechol oxidase: mechanistic studies

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List of publications

- 1) Koval, I. A., Yatsimirsky, K. B., Trofimenko, S., Pavlishchuk, V. V., “Directed synthesis, spectral and magnetochemical characteristics of the new multispin ($S=7/2$, $T = 292$ K) trinuclear complex” Teoreticheskaya i Eksperimentalnaya Khimiya, **1998**, 34, 351-354 (in Russian)
- 2) Pavlishchuk, V. V., Koval, I. A., Goreshnik, E., Addison, A. W., van Albada, G. A., Reedijk, J., “The first example of a true “Turnbull's Blue” family compound with trapped iron oxidation states” Eur. J. Inorg. Chem., **2001**, 297-301
- 3) Schuitema, A. M., Engelen, M., Koval, I. A., Gorter, S., Driessen, W. L., Reedijk, J., “New didentate bispyrazole ligands forming uncommon eight-ring chelates with divalent copper, zinc and cobalt” Inorg. Chim. Acta, **2001**, 324, 57-64
- 4) Koval, I. A., Schuitema, A. M., Driessen, W. L., Reedijk, J., “Unprecedented copper(II)-assisted acetal formation of a formyl-substituted bispyrazole. The X-ray structures of copper[1,2-bis(3'-dimethoxymethylpyrazol-1'-yl)ethane] dichloride and dibromide” J. Chem. Soc., Dalton Trans., **2001**, 3663-3667
- 5) Koval, I. A., Gamez, P., Roubeau, O., Driessen, W. L., Lutz, M., Spek, A. L., Reedijk, J., “Century-known copper salt Cu(OAc)(OMe) proven to be a unique magnetic lattice composed of tetranuclear copper(II) species with a rare binding mode of the acetate anion” Inorg. Chem., **2003**, 42, 868-872
- 6) Koval, I. A., Pursche, D., Stassen, A. F., Gamez, P., Krebs, B., Reedijk, J., “The dicopper(II) complex of the novel asymmetric dinucleating ligand Hpy3asym as a structural model of catechol oxidase” Eur. J. Inorg. Chem., **2003**, 1669-1674
- 7) Schuitema, A. M., Aubel, P. G., Koval, I. A., Engelen, M., Driessen, W. L., Reedijk, J., Lutz, M., Spek, A. L., “Dinuclear copper(II) complexes of four new pyrazole-containing macrocyclic ligands are active catalysts in the oxidative coupling of 2,6-dimethylphenol” Inorg. Chim. Acta, **2003**, 355, 374-385
- 8) Koval, I. A., Huisman, M., Stassen, A. F., Gamez, P., Lutz, M., Spek, A. L., Pursche, D., Krebs, B., Reedijk, J., “New dinuclear Co(II) and Mn(II) complexes of the phenol-based compartmental ligand containing formyl and amine functions: structural, spectroscopic and magnetic properties” Inorg. Chim. Acta, **2004**, 357, 294-300
- 9) Koval, I. A., Huisman, M., Stassen, A. F., Gamez, P., Lutz, M., Spek, A. L., Reedijk, J., “Unusual Cu^{II} and Mn^{II} complexes of phenol-based ligands containing amine, pyridine and formyl functions: Unexpected structural features and solution studies” Eur. J. Inorg. Chem., **2004**, 591-600
- 10) Song, Y. F., Koval, I. A., Gamez, P., van Albada, G. A., Mutikainen, I., Turpeinen, U., Reedijk, J., “Solution studies and structure of a dinuclear-based double-stranded helicate of [Cu-2(p-xysal)(2)] (H-2-p-xysal = bis (hydroxylbenzyl)diaminoxylene)” Polyhedron, **2004**, 1769-1775
- 11) Gamez, P., Koval, I. A., Reedijk, J., “Bio-mimicking galactose oxidase and hemocyanin, two dioxygen-processing copper protein” Dalton Trans., **2004**, 4079-4088
- 12) Song, Y. F., Massera, C., Quesada, M., Koval, I. A., Gamez, P., Lanfredi, A. M. M., Reedijk, J., “A new trinuclear linear copper(II) complex: Unusual crystal structure with semi-coordinated thiophene moieties and weak antiferromagnetic coupling through the bridging imidazolate rings” Eur. J. Inorg. Chem., **2004**, 4566-4571

- 13) Koval, I. A., Huisman, M., Stassen, A. F., Gamez, P., Roubeau, O., Belle, C., Pierre, J.-L., Saint-Aman, E., Luken, M., Krebs, B., Lutz, M., Spek, A.L., Reedijk, J., “*Dinuclear Cu^{II} complexes with a new phenol-based ligand bearing pyridine and thiophene substituents: Synthesis, characterization and interaction with catechol substrates*” Eur. J. Inorg. Chem., **2004**, 4036-4046
- 14) Kozlevčar, B., Golobic, A., Gamez, P., Koval, I. A., Driessen, W. L., Reedijk, J., “*A tridentate bis(pyrazolyl) ligand binds to Cu(II), without using the pyrazole group: a very unusual coordination mode of the ligand Hbdmpb, 1,3-bis(3,5-dimethylpyrazol-1-yl)-2-butanolic acid*” Inorg. Chim. Acta, **2005**, 358, 1135-1140
- 15) Koval, I. A., van der Schilden, K., Schuitema, A. M., Gamez, P., Belle, C., Pierre, J.-L., Luken, M., Krebs, B., Roubeau, O., Reedijk, J., “*Proton NMR spectroscopy and magnetic properties of a solution-stable dicopper(II) complex bearing a single μ -hydroxo bridge*” Inorg. Chem., **2005**, 44, 4372-4382
- 16) Tanase, S., Koval, I. A., Bouwman, E., de Gelder, R., Reedijk, J., “*Ligand conformation enforces trigonal bipyramidal coordination geometry in a new dinuclear bis(pyrazolato)-bridged copper(II) complex: synthesis, crystal structure, and properties of [Cu₂(Npy₂pz)]₂·2CH₃CN*” Inorg. Chem., **2005**, 44, 7860-7865
- 17) Huisman, M., Koval, I. A., Gamez, P., Reedijk, J., “*Thiophene-containing dinucleating ligands for the copper-catalyzed oxidative coupling of 2,6-dimethylphenol*” Inorg. Chim. Acta, **2005**, in press
- 18) Koval, I. A., Belle, C., Selmečzi, K., Philouze, C., Saint-Aman, E., Schuitema, A. M., Gamez, P., Pierre, J.-L., Reedijk, J., “*Catecholase activity of a μ -hydroxidocopper(II) macrocyclic complex: structures, intermediates and reaction mechanism*” J. Biol. Inorg. Chem., **2005**, 10, 739-750
- 19) Koval, I. A., Sgobba, M., Huisman, M., Lüken, M., Saint-Aman, E., Gamez, P., Krebs, B., Reedijk, J., “*A remarkable anion effect on the crystal packing of two analogous copper complexes from a thiophene-containing phenol-based ligand*” New J. Chem., submitted
- 20) Koval, I. A., Selmečzi, K., Belle, C., Philouze, C., Saint-Aman, E., Schuitema, A. M., van Vliet, M., Gamez, P., Roubeau, O., Lüken, M., Krebs, B., Lutz, M., Spek, A. L., Pierre, J.-L., Reedijk, J. “*Catecholase activity of a copper(II) complex with a macrocyclic ligand: unraveling catalytic mechanisms*” Chem. Eur. J., submitted
- 21) Koval, I. A., Gamez, P., Belle, C., Selmečzi, K., Reedijk, J., “*Synthetic models of the active site of catechol oxidase: mechanistic studies*” Chem. Soc. Rev., submitted

Curriculum Vitae

The author of this thesis was born in Kyiv, Ukraine, on 24th October 1979. In 1996, she has graduated from the Technical Lyceum at Kyiv National Technical University, with a major in chemistry and biology. The same year she enrolled as a student at the Chemistry Department at Kyiv National Taras Shevchenko University, from which she obtained her B.Sc. degree (cum laude) in 2000. Her B.Sc. thesis titled “Directed synthesis of ferrocyanide(III)-based polynuclear 3d metal complexes as molecular magnets” was written under supervision of Dr. Vitaly V. Pavlishchuk at the Institute of Physical Chemistry of the National Academy of Science of Ukraine in Kyiv. In June 2000, she has started her M.Sc. studies at Leiden University, The Netherlands, and received her M.Sc. diploma in August 2001, with a M.Sc. thesis “Copper(II) complexes with pyrazole-containing ligands as synthetic models for dinuclear copper-containing proteins” completed under supervision of Dr. Anna M. Schuitema, Dr. Willem L. Driessen and Prof. Dr. Jan Reedijk.

In February 2002, the author has started to work on the Ph.D. thesis in the group of Coordination and Bioinorganic Chemistry (CBAC) at Leiden University, under supervision of Prof. Dr. Jan Reedijk and Dr. Patrick Gamez. In the course of her research, collaboration between CBAC and LEDSS and LEOPR groups at Université J. Fourier, Grenoble, France was initiated. Consequently, the author has visited Université J. Fourier four times in the period of 2003-2005. In 2004, this joined research project has been awarded a collaborative travel grant from the French Ministry of Research and Foreign Affairs (EGIDE) and NWO (Van Gogh Program), allowing visits and exchanges between Leiden and Grenoble.

The results reported in this thesis were presented at various international conferences, such as the 35th and 36th International Conferences on Coordination Chemistry (Heidelberg, Germany, 2002, and Mérida, Mexico, 2004, poster presentations), the 12th International Conference on Bioinorganic Chemistry (Ann Arbor, Michigan, USA, 2005, poster presentation), the 2nd, 4th and 5th Netherlands’ Catalysis and Chemistry conferences (Noordwijkerhout, The Netherlands, 2002, 2004 and 2005, poster and oral presentations), HRSMC meeting (Leiden, 2003, oral presentation), NRSC workshop (Amsterdam, The Netherlands, 2004, oral presentation), and a Combined workshop of NIOK and NRCS-Catalysis (Utrecht, The Netherlands, 2005, oral presentation).

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I am also very grateful to Annemarieke Schuitema-Kamans, who was my supervisor during my M.Sc. research project at CBAC. Annemarieke has taught me a great deal of organic synthesis, and her work with macrocyclic ligands has formed a solid basis, on which I could build my own research.

The crystallographers Dr. Martin Lutz of Utrecht University, Dr. Christian Philouze of Université J. Fourier, Grenoble, and Daniel Pursche and Matthias Lüken of Westfälische Wilhelms-Universität Münster have solved the crystal structures, reported in this thesis. My ex-colleagues Arno Stassen and Olivier Roubeau provided a lot of help with the magnetic susceptibility studies. Gé van Albada’s advice was of a great value when performing EPR experiments, and Lies Bouwman has taught me the simulation of EPR spectra. 13 K EPR measurements in Grenoble were performed with a kind assistance of Dr. Stéphane Ménage

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It is a very special tradition that during your Ph.D. defense, two people stand next to your side: your moral support and reassurance. So I would like to thank two very dear friends, one from Ukraine and one from Holland, Anya Kalayda and Kristel Flinzner, for being my paranymphs.

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