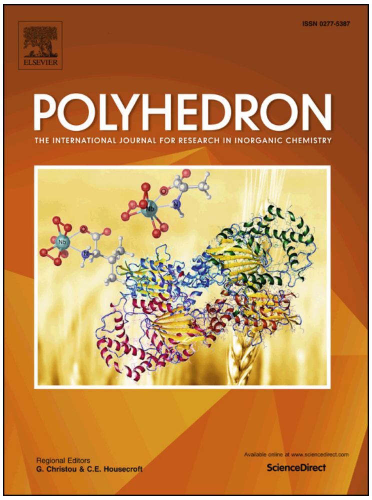

Unpredicted concurrency between P,P-chelate and P,P-bridge coordination modes of 1,5-diR-3,7-di(pyridine-2-yl)-1,5-diaza-3,7-diphosphacyclooctane ligands in copper(I) complexes.

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PII: S0277-5387(17)30634-4
DOI: https://doi.org/10.1016/j.poly.2017.09.047
Reference: POLY 12857

To appear in: *Polyhedron*

Received Date: 31 July 2017
Accepted Date: 30 September 2017

Please cite this article as: I.D. Strelnik, I.R. Dayanova, D.B. Krivolapov, I.A. Litvinov, E.I. Musina, A.A. Karasik, O.G. Sinyashin, Unpredicted concurrency between P,P-chelate and P,P-bridge coordination modes of 1,5-diR-3,7-di(pyridine-2-yl)-1,5-diaza-3,7-diphosphacyclooctane ligands in copper(I) complexes., *Polyhedron* (2017), doi: https://doi.org/10.1016/j.poly.2017.09.047

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Several new mono- and binuclear copper(I) complexes of pyridyl containing 1,5-diaza-3,7-diphosphacylcooctanes with bis-P,P-chelate and unusual P,P-bridged coordination modes of heterocyclic ligands were obtained and characterized. The 1,5-diaza-3,7-diphosphacyclooctane, containing p-tolyl substituents at nitrogen atoms forms bis-P,P-chelate mononuclear as well as metalacyclic binuclear complexes with P,P-bridged coordination mode of a ligand, whereas the N-1-phenylbezyl substituted ligand gives the expected P,P-chelate complexes only. Reasons for the differences in coordination modes have been found in the ligands geometry, where configuration of nitrogen atoms plays an important role.

Introduction

The 1,5-diaza-3,7-diphosphacyclooctanes are a convenient templates for the targeted design of the wide row of the chelate transition metal complexes[1–8]. The diazadiphosphacyclooctanes become the templates for watersoluble and chiral transition metal complexes as well as for the effective catalysts[7,9–13]. Recent works display the diazadiphosphacyclooctanes as excellent candidates for the construction of the gold(I) and copper(I) complexes with “stimuli-responsive” luminescence[14,15].

The search of the biomimetic analogs of the hydrogenase defined the main role of the diazadiphosphacyclooctaanes as ligands for the design of Ni(II) catalysts of the electrochemical hydrogen production[11,16–20]. The research of the mechanisms of the catalytic reactions stimulate the interest to the conformational and coordination behavior of these heterocyclic ligands[5,21]. The behavior of complexes in solution, including the transformations of the geometry of the central metal ion and of the conformational changes of the heterocyclic ligands, was well studied. In all cases the 1,5-diaza-3,7-diphosphacyclooctanes were strongly considered only as a P,P-chelate ligands, which are able to form mononuclear complexes[22–27], whereas the formation of the metalacyclic binuclear species with a bridging coordination mode of the 1,5-diaza-3,7-diphosphacyclooctanes have not even been expected.

Despite of the rich diversification of properties of the diazadiphosphacyclooctanes, their complexation properties to other metal ions are presented poorly, only few works describing the synthesis and structure of the copper(I)[28–30] and the gold(I) complexes[14,15] with 1,5-diaza-3,7-diphosphacyclooctane ligands are published so far.

Herein we report the synthesis of the novel mononuclear bis- P,P-chelate copper(I) complexes of 1,5-diaza-3,7-diphosphacyclooctanes and their binuclear species with P,P-chelate and P,P-bridge coordination modes of ligands, where the “twist-like” conformation of 1,5-diaza-3,7-diphosphacyclooctane is firstly determined by X-ray analysis. The binuclear copper(I) complex with P,P-bridging coordination mode of a ligand represents the first example of the metalacyclic binuclear complex based on 1,5-diaza-3,7-diphosphacyclooctanes.

Materials and methods

All reactions and manipulations were carried out under dry argon with standard vacuum line techniques. Solvents were purified, dried, deoxygenated and distilled before use.

ESI measurements were performed using an AmaZon X ion trap mass spectrometer in positive mode. The mass spectral data were processed using the program XCalibur. The mass spectra are given as m/z values and relative intensities (Irel, %). MALDI mass spectra were obtained on a Bruker ULTRAFLEX III mass spectrometer (laser Nd: YAG, λ 355 nm) in a linear mode without accumulation of mass spectra. ^{1}H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker Avance-DRX 400 spectrometer. Chemical shifts are given in parts per million relative to $SiMe_4$ (^{1}H, internal solvent), and 85% H_3PO_4 (^{31}P, external). J values are given in Hz. The numeration of protons is given on scheme 1.

Data of 4-6 were collected on a Bruker Smart Apex II CCD diffractometer using graphite monochromated MoKα (λ = 0.71073 Å) radiation and ω-scan rotation. Data collection images were indexed, integrated, and scaled using the APEX2 data reduction