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QTAIM study of transition metal complexes with cyclophosphazene-based multisite ligands II. Cobalt(II) complexes

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Dedicated to Professor Vladimír Kvasnička
in honour of his 70th birthday.

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ABSTRACT

$[(CoLCl)CoCl_3]$, $[(CoMeLCl)CoCl_3]$, $[(CoLBr)CoBr_3]$, $[CoLBr]^+$ and $[CoMeLBr_2]$ complexes, L = hexakis(2-pyridyloxy)cyclotriphosphazene, MeL = hexakis(4-methyl-2-pyridyloxy)cyclotriphosphazene, in the most stable high spin states are investigated at DFT level of theory using hybrid B3LYP functional. The exchange coupling parameter evaluated using a broken symmetry treatment increases with the ligands mass. Electron density is evaluated in terms of QTAIM (Quantum Theory of Atoms-in-Molecule) topological analysis of electron density. The bonds of central Co atoms with phosphazene nitrogens are shorter, stronger and more polar than with the aromatic pyridine nitrogens and their higher ellipticities may be explained by the π contribution from the phosphazene ring. The atomic charges of phosphazene nitrogens are ca. twice more negative than at the pyridine ones.

1. Introduction

The phosphazene backbone consists of alternating phosphorus and nitrogen atoms with formally alternating single and double P–N bonds. Cyclic phosphazenes play the most important role in understanding the nature of this type bonding and serve as model compounds for new polyphosphazene polymeric materials. Old models of phosphazene bonding proposed by Craig and Paddock [1] and Dewar et al. [2] used the 3d and 2p orbitals on the phosphorus and nitrogen atoms, respectively, to form π-bonds. Nevertheless, quantum chemical calculations show that phosphorus 3d orbitals cannot play a significant role in phosphazene–nitrogen bonding. Using mathematical apparatus of group theory it may be exactly shown that the p(N)–d(P) bonding interaction is symmetrically forbidden in the cyclophosphazene rings of D_{nh} symmetry with odd n [3]. The recent model is based on predominantly ionic P–N bonds with a negative hyperconjugation component [4]. P–N bonds in cyclophosphazene rings with various ligands have been analysed in the terms of QTAIM (Quantum Theory of Atoms-in-Molecule) topological analysis of electron density [5–9].

Cyclophosphazenes with pendant donor groups attached to the phosphorus atoms exhibit diverse behaviour as multimodal ligands for transition metal ions [10]. A wide variety of donor groups can be readily attached to the cyclotriphosphazene platform via nucleophilic substitution reactions with primary and secondary amine, alcohol and phenol groups that incorporate appropriate donor atoms such as nitrogen. For the sake of simplicity we will restrict to hexakis(2-pyridyloxy)cyclotriphosphazene (L), hexakis(4-methyl-2-pyridyloxy)cyclotriphosphazene (MeL), octakis(2-pyridyloxy)cyclotetraphosphazene (L′) and octakis(4-methyl-2-pyridyloxy)-cyclotetraphosphazene (MeL) which have been used to form a diverse range of complexes with zinc(II), copper(II), nickel(II) and cobalt(II) halides [11–14]. The incorporation of the flexible pyridyloxy pendant arms facilitates the binding of the metal ion to the less basic phosphazene ring nitrogen atoms and allows the formation of six-membered chelate rings without significantly distorting the planarity of the P_3N_3 ring. $[MeL'(CuCl_2)_2]$, $[L'(CuBr_2)_2]$ and $[MeL'(CuBr_2)_2]$ complexes form discrete dimetallic cyclotetraphosphazene-based moieties and exhibit normal Curie-like susceptibilities [14].

The above mentioned compounds are very suitable for the comparative studies of the different bonding of phosphazene and pyridine nitrogens with transition metal ions. There are only few theoretical studies dealing with this type complexes at DFT level of theory using hybrid B3LYP functional. Free mono- and disubstituted phenoxy-cyclophosphazenes have been investigated at Hartree-Fock and/or DFT levels of theory [8,15].

Ainscough et al. [14] reported the calculations of the dimetallic complexes, $[MeL(CuCl_2)_2]$ and $[MeL'(CuCl)_2]^{2+}$, and identified “electron-density-bridge” molecular orbitals which involved Cu 3d orbitals overlapping with the non-bonding, N-based molecular

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orbitals on the phosphazene rings as the pathway for the weak antiferromagnetic coupling observed between the copper(II) centres (by N–P═N or N–P═N–P═N phosphazene bridges).

In the first part of our study [16] the metal–ligand bonds in dimetallic [$(ZnCl_2)_2L$] complex, six-coordinate [NiLCl]$^+$ and green-[$NiLCl_2$] complex as well as five-coordinate red-[$NiLCl_2$] complex have been investigated. Electron density has been evaluated in the terms of QTAIM (Quantum Theory of Atoms-in-Molecule) topological analysis of electron density. The bonds of central transition metal atoms with phosphazene nitrogens are shorter, stronger and more polar than these ones with the aromatic pyridine nitrogens and thus their high ellipticity might be explained by π bond contribution from the phosphazene ring rather than by mechanical strain. The atomic charges of phosphazene nitrogens are ca. twice more negative than of the pyridine ones. Unlike Zn(II) complexes, the Ni(II) ones prefer higher spin states (paramagnetic compounds).

In [17] the metal–nitrogen bond in six-coordinate complexes green-[$NiLCl_2$] and [MLCl]$^+$ with M = Co, Ni, Cu or Zn, five-coordinate complexes red-[$NiLCl_2$] and [$MLCl_2$] with M = Cu or Zn, and dimetallic complexes [$MeL(CuCl_2)_2$], [$MeL'(CuCl)_2$]$^{2+}$ and [$MeL'(CuCl_2)_2$] has been investigated using natural bond orbital (NBO) analysis. The calculations show that the phosphazene ring nitrogen acts as a σ donor and divalent metal ions bind to the phosphazene ring nitrogen by a σ-type bond. The lengthening of the P–N bonds, which flank the metal coordination site, can be explained as a result of electron density that is transferred from P–N bonding orbitals to the 4s orbital of the metal ion rather than a decrease in the π component of the bond as suggested by earlier models [1,2]. The ionic component of the P–N bond is reduced upon metal coordination in agreement with [4].

Magnetic properties can be explained in the terms of the Heisenberg – Dirac – van Vleck model of an isotropic interaction between paramagnetic centres A and B

$$H = -2J \cdot S_A \cdot S_B \tag{1}$$

where S_A and S_B are the local spin operators for each of the paramagnetic centres and J is the Heisenberg exchange coupling parameter. A post Hartree-Fock treatment is necessary to obtain a quantitative agreement with the experimental J value. The broken symmetry (BS) approach [18,19] relates the energy of a BS single determinant (SD), which is not an eigenstate of the S^2 operator, to the energy of a pure spin state. The spin state of the highest multiplicity (HS) is almost a pure one and can always be correctly described by a SD whereas the lower spin states are usually contaminated by the higher spin state components. The BS state is constructed in order to obtain an electronic symmetry which is lower than the actual nuclear symmetry (in order to allow the two magnetic orbitals to interact by using different orbitals for different spins α and β). The two different orbitals which accommodate electrons with different spins (spin polarised calculation) are usually located on each centre in order to have the maximum local spins and are coupled together in order to have the minimum resulting spin (a globally antiferromagnetic state where the spin α and β density is localised on different paramagnetic centres). From a computational point of view, the use of BS wavefunctions is particularly convenient because the BS state energy can be obtained through a simple SCF procedure while the energy of any intermediate spin state would need a multiconfigurational procedure.

For a binuclear system, Noodleman et al. [18,19] derived the expression

$$J = -\frac{E_{HS} - E_{BS}}{\langle S^2 \rangle_{HS} (s_{AB}^2 + 1)} \tag{2}$$

where E_Y is the energy of the spin state Y (Y = HS or BS), $\langle S^2 \rangle_{HS}$ is the expectation value of the spin-squared operator at HS state and s_{AB} is the overlap between the HS magnetic orbitals ($s_{AB} = 0$ corresponds to a weak bonding limit and $s_{AB} = 1$ to a strong bonding limit between magnetic centres A and B).

A modification of this approach using the approximate spin projection (AP) treatment leads to the relation [18,20,21]

$$J = -\frac{E_{HS} - E_{BS}}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}} \tag{3}$$

where E_Y and $\langle S^2 \rangle_Y$ denote the energy and the expectation value of the spin-squared operator, respectively, at the spin state Y (Y = HS or BS).

The aim of our study is to extend the theoretical studies in [16] to Co complexes with hexakis(2-pyridyloxy)cyclotriphosphazene (L) and hexakis(4-methyl-2-pyridyloxy)-cyclotriphosphazene (MeL) ligands synthesized in [13]. We will focus on their magnetic properties as well (despite not measured till now).

2. Method

In the first step, the hydrogen atoms positions in the experimental geometries of the complex compounds under study are optimised by molecular mechanics (MM+ method) [22]. Then the electronic structure of these complexes is evaluated at DFT level of theory using hybrid B3LYP functional with 6-311G basis set for Co, 6-31G* bases for P, Cl and Br and 6-31G bases from Gaussian library [23] for the remaining atoms. Gaussian03 software [23] is used for single-point calculations. The systems studied in BS singlet states are calculated using an unrestricted formalism (keyword Guess = Mix).

The electronic structure of the species under study is investigated using QTAIM (Quantum Theory of Atoms-in-Molecule) topological analysis of electron density [24]. The results are evaluated in the terms of atomic volumes V and atomic charges q obtained using the electron density integrated over atomic basins (up to 0.001 e/Bohr^3 level). Bond characteristics are evaluated in terms of electron density ρ, its Laplacian $\nabla^2\rho$

$$\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3 \tag{4}$$

and bond ellipticity ε

$$\varepsilon = \lambda_1/\lambda_2 - 1 \tag{5}$$

at bond critical points (BCP) where $\lambda_1 < \lambda_2 < 0 < \lambda_3$ are the eigenvalues of the Hessian of the BCP electron density.

AIM2000 [25] software package is utilised for QTAIM analysis of Gaussian03 results. MOLDRAW 2.0 software [26] is used for visualisation and geometry manipulation purposes.

3. Results

We have investigated the following Co(II) complexes with L = hexakis(2-pyridyloxy)cyclotriphosphazene or MeL = hexakis(4-methyl-2-pyridyloxy)cyclotriphosphazene in experimental geometries [13] with corrected H positions:

(I) Neutral dimetallic complex [$(CoLCl)CoCl_3$] (model A) with six-coordinate (κ^5N tetrapodal L binding mode) and four-coordinate (κ^1N monodentate L binding mode) Co(II) centres (Fig. 1).

(II) Neutral dimetallic complex [$(CoMeLCl)CoCl_3$] (model B) with six-coordinate (κ^5N tetrapodal MeL binding mode) and four-coordinate (κ^1N monodentate MeL binding mode) Co(II) centres (Fig. 2).

(III) Neutral dimetallic complex [$(CoLBr)CoBr_3$] (model C) with six-coordinate (κ^5N tetrapodal L binding mode) and four-coordinate (κ^1N monodentate L binding mode) Co(II) centres (Fig. 3).