DFT modelling of cobalt and nickel complexes with dithiophosphinic acid

Alexis Otero-Calvi [a], Luís A. Montero [b,*], Wolf-Dieter Stohrer [c]

[a] *Departamento de Química, Instituto Superior Minero Metalúrgico, Moa 83329, Holguín, Cuba*
[b] *Laboratorio de Química Computacional y Teórica, Facultad de Química, Universidad de La Habana, Habana 10400, Cuba*
[c] *Institute of Organic Chemistry, University of Bremen, Leobener Straße, D-28334 Bremen, Germany*

ARTICLE INFO

ABSTRACT

Calculations based on density functional methods are carried out for the dithiophosphinate cobalt and nickel complexes. An interpretation of the electronic structure of these complexes is made according Mulliken and Natural Population Analysis together with the Atoms in Molecules approach showing the kind of main interactions between metals and the ligand. Results show that the M–L bond is mainly governed by charge transfer from the ligand to the metal atom by the participation of the sulfur lone pair with similar covalent contribution for cobalt and nickel in case of octahedral complexes. In the case of tetrahedral cobalt complex they have a relative higher contribution with respect to the last. The calculated interaction energy confirms the preference for the formation of the tetrahedral cobalt complex if we take into account the low values of the frontier molecular orbital as it is shows by the molecular orbital analysis. The small difference in the interaction energy between tetrahedral and octahedral cobalt complexes gives possibilities for the formation of octahedral complexes.

1. Introduction

Dithiophosphorus ligands are known as excellent chelating agent in areas such as liquid–liquid extraction of metal ions from aqueous solutions. Some investigations confirm that, in general, the separation factor is ordered according the series: phosphoric < phosphonic < phosphinic [1,2]. Comparisons of the extractions qualities of these reagents have been documented by Preston [3] and others [4,5] showing the efficiency in the separation with phosphinic acids. An example of the studies about the separation of nickel and cobalt ion with these reagents is performed by Tait [5], Bourget [6], Sole [4] and others [7,8].

Their results confirm the selectivity order as dithiophosphinic > monothiophosphinic > phosphinic acids in agreement with the Hard–Soft Acid–Base (HSAB) concept [9]. Complexation of soft Lewis acids, such as Ni and Co ions, with a soft Lewis base should occur with high selectivity. Given the fact that in the most common Lewis bases the donor atoms have electronegativities increasing in the order S < Br < N < Cl < O < F, a substitution of oxygen by a sulfur atom must favor the separation of these two metals.

If the extraction were to occur by a simple cation exchange, the extraction for a divalent cation, such as Co^{2+} or Ni^{2+}, during the separation process would be:

$$2HA_{(org)} + M^{2+}_{(aq)} = MA_{2(org)} + 2H^+_{(aq)} \qquad (I)$$
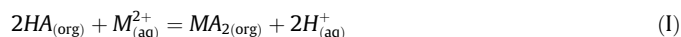
However, in this process, the extractants are polymerized or self-associated in the organic solvent [5], mostly in the case of phosphinic acid, a consequence of a hydrogen bond. It is supported by the experimental studies on the gas phase IR spectrum of dimethylphosphinic acid, that shows the existence of very strong hydrogen bond within the dimer [10].

In the case of dithiophosphinic acid the results [5] show that the cobalt complexes have tetrahedral configuration and the nickel complexes have octahedral configuration. Based in the reaction mechanism and taking into account the equilibrium process it has been proposed that the species formed are CoA_2 and $NiA_2(H_2O)_2$ (A = bidentate ligand) [4] and that the selectivity order favors the separation of cobalt.

In our previous paper [11], we report a theoretical study on the molecular structure of dithiophosphorus nickel complexes, reporting DFT calculations on several model compounds and analyzing bonding therein in order to understand the effect of the substituent on the charge distribution. In this case, we report a comparison between the molecular structure of octahedral nickel complexes and the cobalt counterparts employing DFT in order to understand the effect of the molecular geometry in the separation process. According to Danesi [12] the selectivity for cobalt or nickel ions is originated by the molecular structure of the complexes. A thermochemical interpretation of the reaction is also considered.

* Corresponding author. Tel.: +53 78781263.
  E-mail address: lmc@fq.uh.cu (L.A. Montero).

2. Computational details

2.1. Models and methods

The models for complexes with dithiophosphinate ligands (Fig. 1) were constructed taking into account the reported complexes for nickel and cobalt [5] during the separation of this metals with a specific solvent, but including octahedral complexes for cobalt atom. Two possible isomers were calculated for octahedral configuration and a tetrahedral complex for cobalt atom. In all cases the high spin structures were considered.

Calculations have been performed by using Kohn-Sham's DFT methods, specifically the gradient-corrected hybrid density functional B3LYP [13–15]. For each considered structure, a full geometry optimization was performed using this functional, that is a combination of the Becke's three-parameter non-local exchange potential with the non-local correlation functional of Lee, Yang and Parr [16,17].

In the first step of our calculation, the 6-31G* [18,19] basis set were chosen for hydrogen, phosphorus, oxygen and sulfur atoms. In the case of nickel and cobalt atoms a non-relativistic effective core potential (ECP) according to Hay and Wadt [20] was used. The valence basis set used in connection with this ECP is essentially of double-ζ quality (LanL2DZ). Frequency calculations on all optimized systems were carried out to characterize stationary point in the potential energy surfaces for each structure. In the second step, the energy is evaluated for the optimized geometries using a large basis set including diffuse and polarization function on each atom (6-311+G(3df,2p)) [21–23]. In the case of metal (M) atom, the same first step conditions were used. This final energy evaluation was performed in a reaction field at the same level of theory and using water as solvent ($\varepsilon = 78.39$). All the calculations are carried out using the Gaussian [24] program.

For the molecular orbital analysis, the program PyMOlyze [25] was used in order to obtain the Mayer bond order (MBO) and the Mulliken population analysis (MPA).

2.2. Charge distribution analysis

The charge distribution analysis was made on the basis of the Natural Population Analysis (NPA) [26–28] using the NBO 3.1 [29] program implemented in the Gaussian package. According to this approach the natural population $q_i^{(A)}$ of orbital $\varphi_i^{(A)}$ on atom A is the diagonal density matrix element in the natural atomic orbital (NAO) basis which may be summed to give the total number of electrons and the natural charge $Q^{(A)}$ on atom A with atomic number $Z^{(A)}$. In conjunction with NPA, the Atoms in Molecules [30] (AIM) approach was used. This method has the potential advantage over other methods based on molecular orbitals that it is concerned with a topological analysis of the electron density that is

a potentially observable property of the molecule. The AIM method achieves the separation of a molecule into regions associated with each atom. The bond critical point is the position along the path between two bonded atoms at which the electron density is a minimum. The values of the density at this point, ρ_b, and the sign of the Laplacian, $\nabla^2(\rho)$, characterize the bond as either a shared or closed shell interaction and indicate the covalency of the interaction. The XAIM [31] software was used to obtain the corresponding values. The Mayer [32,33] bond order was calculated too. This quantity is a generalization of the Wiberg [34] bond index for non-orthogonal basis set. In the case of a bond between two atoms A and B, it is given by

$$B_{AB} = \sum_{\lambda \in A} \sum_{\lambda \in B} (PS)_{\omega\lambda}(PS)_{\lambda\omega} \qquad (1)$$

from Ref. [32] where P and S are the density and overlap matrices and the summations run over the atomic orbitals on the two atoms. The Mayer bond order is related to the number of shared electron pairs between the atoms. This leads to the classical integer values for homonuclear diatomics. Non-integer values reflect the ionic character of the bonds as well as delocalization and multicenter effects. The insight obtained with the Mayer bond order for transition metal compounds has been demonstrated by some cases of study [35–37].

3. Results

3.1. Geometrical parameters

Geometrical parameters of the global minima in the potential energy surfaces for the calculated complexes are summarized in Table 1. The cobalt atom in the model 1 is four-coordinated by sulfur atoms with D_{2d} symmetry. The calculated geometry of this model (tetrahedral cobalt complexes) shows deviations in the SCoS

Table 1
Geometrical parameters for the optimized geometries (Å)

Compounds	d(M–S)	d(P–S)	d(M–O)
H$_2$PSS$^-$	–	2.018	–
1	2.439	2.038	–
2a	2.490; (2.668)	2.044; (2.022)	2.165
3a	2.584	2.033	2.159
2b	2.544; (2.555)	2.032; (2.033)	2.130
3b	2.550	2.032	2.120

d, bond distance between the Metal (M); phosphorus (P); sulfur (S) and oxygen (O) atoms.

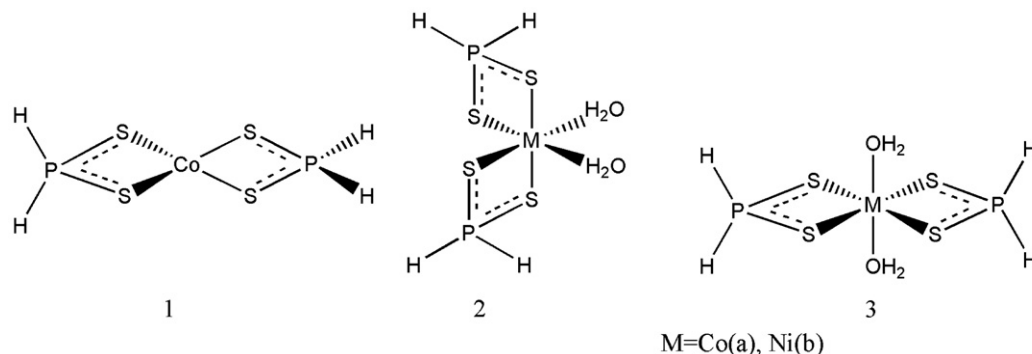In parentheses the value corresponding to the sulfur atom in axial position for the *cis* isomer.

Fig. 1. Calculated nickel and cobalt complexes with dithiophosphinic acid.