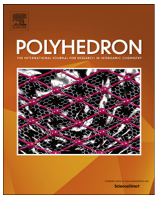
Polyhedron 110 (2016) 46–54

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Nature of the metal–ligand bond in some $[(CO)_4M \leftarrow BIIM(R)]$ {M = Cr, Mo, W; R = H, F, Cl, Br} complexes: A theoretical study

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ARTICLE INFO

Article history:
Received 4 January 2016
Accepted 5 February 2016
Available online 16 February 2016

Keywords:
Metal–ligand bond
DFT
Orbital interaction
EDA
ETS-NOCV

ABSTRACT

A theoretical study on the structure and nature of the M ← N bond in some potential pharmacologically active complexes; $[(CO)_4M \leftarrow BIIM(R)]$ {M = Cr, Mo and W, R = H, F, Cl and Br} with R(3,3 substitution), R(4,4 substitution), R(5,5 substitution) and R(3,3 4,4, 5,5 substitutions) was carried through density functional BP86 and *ab initio* MP2 methods using the def2-TZVPP basis set. The M ← N bond was analyzed using NBO, AIM, EDA and ETS-NOCV to obtain the electrical charge and energy decomposition analysis (EDA). The results showed that $[(CO)_4W \leftarrow BIIM(H)]$ and $[(CO)_4Cr \leftarrow BIIM(F)]$ are related to the D form complex with the biggest and the smallest ΔE_{int}, respectively. Additionally, the M ← N bond interaction energies (ΔE_{int}) increase in the group from top to bottom, from the lighter to the heavier elements (Cr < Mo < W). The EDA suggests that the $[(CO)_4M \leftarrow BIIM(R)]$ attractive interactions come mainly from ΔE_{elstat}, which provides ~60% of ΔE_{int}, while ~40% comes from ΔE_{orb}. The applicability of the ETS-NOCV scheme is demonstrated for the complexes and it is shown that the ΔE_{orb} term arises mainly through $[(CO)_4M \leftarrow BIIM(R)]$ σ-donation (in the range 54–61%) while a smaller part (~27%) comes from $[(CO)_4M \rightarrow BIIM(R)]$ π-back donation. The nature of the M ← N bond in the complexes was also studied by AIM and NBO analyses. The data has confirmed that the M ← N bond is partly covalent.

1. Introduction

In recent years, 2,2″-biimidazoles (BIIMs) have attracted much attention due to their biological applications [1–10] and also for the coordination chemistry of metal complexes of 2,2″-biimidazoles with main group transition metal atoms. Classically, 2, 2′-biimidazoles are known for their ability to act as bi-dentate, tri-dentate and tetra-dentate ligands, being capable of stabilizing both homonuclear and heteronuclear metal complexes [11]. The important role of imidazole and its derivatives both in the field of biologically active compounds and in organic synthesis is well documented [12].

There are several reports about the coordination chemistry of metal complexes of BIIM, with main group and transition metal ions in an octahedral geometry [13–18]. Beck and his co-workers reported the synthesis and spectroscopic characterization of tetracarbonyl complexes of $[LM(CO)_4]$ (L = BIIM and M = Cr, Mo and W) [16]. Casas and co-workers prepared and tested biological activity of tin(IV) complexes of BIIM and its derivatives, then they synthesized Pd(II) and Pt(II) complexes of BIIM and its derivatives, which were characterized spectroscopically; they have also looked at some properties, such as interactions with DNA [17]. Sordo and et al. have reported the isolation and characterization of $[SnMe_2X_2(DM\ BIIM)]$ (X = Cl or Br; DM BIIM = N,N′-dimethyl-2, 2″-biimidazole). Also the structure of $[SnMe_2Br_2(DM\ BIIM)]$ was determined by X-ray diffraction [18].

Recently a quantitative estimate of the strength of M ← L σ donation and M → L back bonding in main group and transition metal complexes with different types of ligands has been made [19–23] with the energy decomposition analysis (EDA) method, which was developed by Morokuma [24] and Ziegler and Rauk [25]. Also Frenking et al. reported several studies on the structures and nature of metal–CO and ligand–M (CO) bonding [26–28]. The EDA method extends the bonding analysis beyond the attractive orbital terms by including electrostatic interactions and Pauli repulsion.

According to our best knowledge, to date there have not been any reports on $M(CO)_4$, (M = Cr, Mo, W) complexes with BIIM(R) = 2,2′-biimidazole derivatives. Herein, we want to report a comparative investigation on the structures and bonding situations of the $[BIIM(R) \rightarrow M(CO)_4]$ (R = H, F, Cl, Br; M = Cr, Mo, W) complexes (see Scheme 1).

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http://dx.doi.org/10.1016/j.poly.2016.02.022
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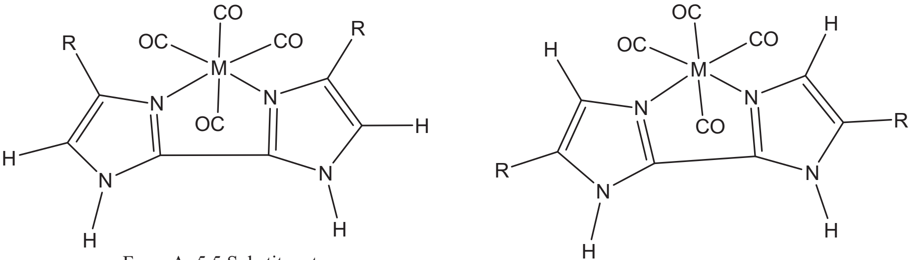


Form A: 5,5 Substituent

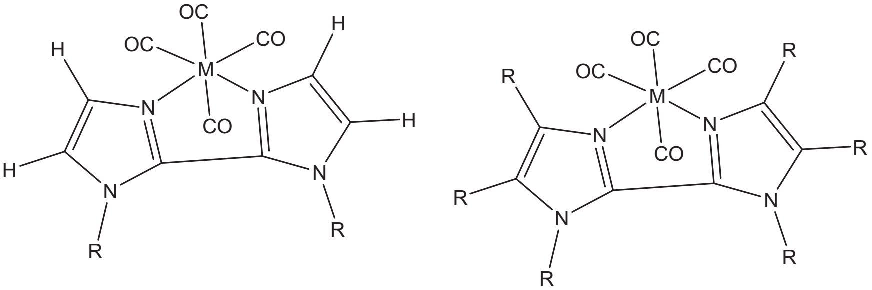
R= F, Cl, Br

M=Cr, Mo, W

Form B: 4,4 Substituent

R = F, Cl, Br

M = Cr, Mo, W



Form C: 3,3 Substituent

R= F, Cl, Br

M= Cr, Mo, W

Form D

R=H, F, Cl, Br

M=Cr, Mo, W

Scheme 1. Schematic representation of the [$(CO)_4M \leftarrow$ BIIM(R)] (M = Cr, Mo, W; R = H, F, Cl, Br) complexes investigated here.

2. Computational details

In recent studies on octahedral hexa-coordinated complexes of main group and transition metal complexes it has been shown that BP86 is suitable level for the calculation of L → M bonding situations in these complexes [22,23,29] and some other complexes [30]. According to this study the geometry optimization of the molecules has been carried out at the BP86 and MP2 levels of theory using the def2-TZVPP basis set. In all cases the vibrational frequency analyses, calculated at the same level of theory, indicate that the optimized structures, which are at the stationary points, correspond to local minima without any imaginary frequencies.

All calculations were performed by using the G03 Program [31]. Natural bond orbital (NBO) analyses [32], with density = current keyword, were also carried out using the internal module GAUSSIAN 03. The AIM2000 package was used to obtain the bond properties. The wave function files were generated from the Gaussian output BP86/def2-TZVPP levels of theory to perform AIM calculations [33]. The program package ADF2009.01 was used for bonding analyses in the terms of energy-decomposition analysis, at BP86/TZP (ZORA)//BP86/def2-TZVPP with C1 symmetry. The basis sets for all the elements were triple-ζ quality augmented by one set of polarization functions (ADF basis set TZP(ZORA)).

3. Results and discussion

3.1. Structural studies

The synthesis and spectroscopic characterization of pharmacological potential of [$(CO)_4M \leftarrow$ BIIM] {M = Cr, Mo and W} complexes were reported in experimental papers by Beck and coworkers, who studied the reactions of [$M(CO)_6$] {M = Cr, Mo and W} with 2,2′-biimidazoles [16]. The authors claimed the formation of the complexes on the basis of ^{1}H NMR and vibrational spectra, though no X-ray structure analysis data was obtained to corroborate this. The most important theoretically calculated bond lengths and bond angles of all the complexes investigated here (See Scheme 1) at the BP86/def2-TZVPP level of theory are shown in Table 1 (the structural data at the MP/def2-TZVPP level of theory are given in the Supporting Information). A comprehensive set of geometrical data is given in the Supporting Information. As it can be seen, the tendency of variation of the M–N bond lengths and N–M–N bond angels of the complexes are Mo–N > W–N > Cr–N and N–Cr–N > N–Mo–N > N–Wr–N (see Scheme 1 and Table 1) respectively. The M–N bond lengths and the N–M–N bond angles in the complexes [$(CO)_4M \leftarrow$ BIIM(R)] {M = Cr, Mo and W; R = H, F, Cl and Br} represent little variation when M remains the same element, indicating that the nature and location of the R substituents have no significant effect on the geometries.

3.2. Interaction energies

The interaction energy (ΔE_{int}) between the studied BIIM(R) and $(CO)_4M$ (M = Cr, Mo, W) fragments in the optimized structures of the [$(CO)_4M \leftarrow$ BIIM(R)] {M = Cr, Mo, W; R = H, F, Cl, Br} complexes were calculated at the BP86 and MP2 levels of theory using the def2-TZVPP basis set. The interaction energies were calculated according to following equation:

$$\Delta E_{\text{int}} = E_{[(CO)_4M \leftarrow BIIM(R)]} - \left(E^{BIIM(R)}_{[(CO)_4M \leftarrow BIIM(R)]} + E^{(CO)_4M}_{[(CO)_4M \leftarrow BIIM(R)]} \right)$$

Here $E^{BIIM(R)}_{[(CO)_4M \leftarrow BIIM(R)]}$ and $E^{(CO)_4M}_{[(CO)_4M \leftarrow BIIM(R)]}$ represent the electronic energies of the interacting fragments in the [$(CO)_4M \leftarrow$ BIIM(R)] complexes.

Table 2 gives the theoretically predicted ΔE_{int} values for all the investigated complexes (form A, B, C and D, see Scheme 1). The