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Review

The role of electronic delocalization in transition metal complexes from the electron localization function and the quantum theory of atoms in molecules viewpoints

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Abbreviations: 2c-2e, two-center two-electron bond; 3c-2e, three-center two-electron bond; 3c-4e, three-center four-electron bond; 5-MR, five-membered ring; 6-MR, six-membered ring; AO, atomic orbital; AOM, atomic overlap matrix; a.u., atomic units; B3LYP, Becke's three parameter nonlocal exchange and Lee–Yang–Parr 1988 nonlocal correlation functional; BP86, Becke's nonlocal exchange and Perdew 1986 nonlocal correlation functional; BCP, bond critical point; CCSD(T), coupled-cluster theory with singles and doubles and non-iterative estimation of triple excitations method; CASSCF, complete active space self-consistent field; DAFH, domain-averaged Fermi hole; DCD, Dewar–Chatt–Duncanson bonding model; DFT, density functional theory; DI, delocalization index; e, electrons; ELF, electron localization function; ESI, electron sharing index; FLU, aromatic fluctuation index; GC, guanine-cytosine base pair; H-bond, hydrogen bond; HF, Hartree–Fock method; HOMA, harmonic oscillator model of aromaticity; l.h.s., left hand side; LI, localization index; MCI, multicenter delocalization index; MO, molecular orbital; MSO, molecular spin–orbital; n-DI, n-center delocalization index; NBO, natural bond orbital; NICS, nucleus independent chemical shift; pd, pentadienylylidene; PDI, *para*-delocalization index; ptC, planar tetracoordinate carbon atom; QTAIM, quantum theory atoms in molecules; r.h.s., right hand side; RCP, ring critical point; TM, transition metal; TZP, triple-zeta plus polarization functions basis set; VSEPR, valence shell electron pair repulsion.

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ABSTRACT

Electronic delocalization is invoked in many textbooks as the driving force of several fundamental phenomena such as conjugation, hyperconjugation, and aromaticity. These phenomena are important to explain structure, stability, and reactivity not only of classical organic compounds but also of many inorganic, organometallic, and all-metal cluster species. There are a number of available theoretical methods to quantify the electron localization/delocalization in molecules. In this review, we concentrate our efforts in the description of those studies that analyze electron delocalization in transition metal complexes employing the two most widespread techniques to measure delocalization: the electron localization function and the electron sharing indices obtained in the framework of the quantum theory of atoms in molecules. While the former enables the localization of regions in the molecular space where electrons concentrate leading to chemically significant regions such as bonds or lone pairs, the latter provides an atomic subdivision of the molecular space where each atom localizes a certain number of electrons. The joint effort of these techniques has already been proven as one of the most powerful methods to understand the chemical bonding. We show that theoretical studies of electron delocalization improve significantly our understanding of the bonding mechanism, structural properties, and reactivity of transition metal species.

1. Introduction

1.1. Importance of TM complexes

Living organisms transport and store transition metals (TMs). Although TM are present in small concentration ranges in biological systems, their importance is capital as they are bound to proteins or found in cofactors such as porphyrins or cobalamins. Iron, well-known for reversible binding of dioxygen (hemoglobin or hemerythrin), copper which participates in activation of dioxygen, cobalt found in vitamin B12 or molybdenum proteins catalyzing the reduction of nitrogen and nitrate are just a few examples which illustrate the importance of TM complexes in biological systems [1]. TMs are also important in a wide range of fields such as catalysis, material synthesis, photochemistry, bioinorganic chemistry and even cancer treatment, as is the case for *cis*-platinum which was shown, in 1965, to prevent cell division [2,3]. The synthesis of new TM complexes is timely and some complexes find striking applications, especially in the field of catalysis. In addition, TM complexes are appealing to the chemists due to the variety of colors exhibited in comparison with complexes formed by the main metals, which are usually white [4].

Due to the size and the number of electrons involved in TM complexes, reliable purely *ab initio* methods are prohibitive and the density functional theory (DFT) methods has had a prominent position in the understanding of TM chemistry [5]. Therefore, the role of the quantum chemistry in the field of TM chemistry has come along with the development of new functionals in the framework of DFT.

1.2. Chemical bonding in TM

TM complexes are species consisting of a TM covalently bonded (coordinated) to one or more molecules or ions (ligands). The formation of the complex can be understood as a Lewis acid, the TM cation, reacting with a Lewis base, the ligand.

The most successful simple model to explain the chemical bonding is perhaps the electron pairing model developed by Lewis, who in addition to his cubic atom theory, gave rise to the well-known octet rule [6]. The octet rule is a rule of thumb which states that atoms tend to combine in such a way that they occupy their valence shells with eight electrons. In TM chemistry there is an analogy to the octet rule, the 18-electron rule, which is used for characterizing and predicting the stability of metal complexes. The origin of this rule comes from the fact that valence shells of a TM can accommodate 18 electrons: 2 in each of the five d orbitals, 2 in each of the three p orbitals and 2 in the s orbital.

In as much as several quantum mechanical concepts such as the electron sharing indices (ESI) [7] or bond orders [8–10] have overcome the octet rule to analyze chemical bonding, several theories have also been defined to improve the picture of the chemical bonding in TM chemistry provided by the Lewis model. The ligand field theory (LFT) is one of the most widely used models, still present in most textbooks that analyze TM chemistry. LFT represents an application of molecular orbital theory (MOT) to TM complexes, and is an improvement over the well-known crystal field theory (CFT), which uses an electrostatic model to explain all metal ion–ligand interactions and was first proposed by Hans Bethe in 1929 [11].

Several quantum chemical tools have been designed to analyze chemical bonding, including the natural bond orbital (NBO) methods [12], the charge decomposition (CDA) [13] or the energy-decomposition analyses (EDA) [14]. For a recent review on the nature of bonding covering some of these aspects in TM compounds see Ref. [15]. The aim of this review is to pursue the study in TM bonding by focusing on the electron delocalization in TM species. Namely, we will analyze the role of two quantum chemical tools, the quantum theory of atoms in molecules (QTAIM) and the electron localization function (ELF), to have a good grasp of the electron delocalization in TM chemistry. We will show through a series of examples how these two approaches can be successfully used to analyze the most fascinating bonding situations encountered in TM chemistry.

1.3. QTAIM and ELF, competing or complementing each other?

Since the appearance of the ELF in the literature in 1990, several researchers [16–19] have deeply analyzed the differences between QTAIM and ELF approaches. So far, the QTAIM has been the preferred quantum mechanical tool to analyze chemical bonding and chemical interactions.

QTAIM, based on the topology of the electron density, enables the partition of the molecular space into atomic regions, giving rise to atomic properties including the atomic population and its statistical interpretation accompanying, as well as a bunch of chemical tools which were used to analyze the chemical bonds: the bond critical point (BCP) and the ring critical point (RCP), the value of the density, the energy density and the Laplacian of the electron density calculated in these points are just a few examples. QTAIM was not exempt of controversy, and some of the issues of the theory, such as the tenet [20] that a BCP and a bond path connecting two