Orbital: The Electronic Journal of Chemistry
journal homepage: www.orbital.ufms.br
e-ISSN 1984-6428

| Vol 10 | | No. 7 | | October-December 2018 |

FULL PAPER

Solvent Effects on Frontier Orbitals and Electronic Transitions of Manganese Carbonyl Complexes: A DFT/TDDFT Study

Elvan Üstün*, Ali Kemal Mehel

Department of Chemistry, Faculty of Art and Science, Ordu University, 52200, Ordu, Turkey

Article history: Received: 10 May 2018; revised: 26 June 2018; accepted: 24 October 2018. Available online: 31 December 2018. DOI: http://dx.doi.org/10.17807/orbital.v10i7.1157

Abstract:

Metal carbonyl complexes constitute a molecular family that is widely used in chemical processes since their discovery. Recently, one of the most popular applications of these molecules is storage/transport of CO. It is known that CO is not only an ordinary toxic gas but also a gasotransmitter. It is synthesized endogenously and the amount of CO increases in healing periods. This knowledge provides strong motivation for using metal carbonyl complexes as CO-releasing molecules for therapeutic purposes. However, the solvent that is used in analyzing CO-releasing properties causes quantitative discrepancies and this is a disadvantage for progression of studies. Nevertheless, it is extremely difficult to analyze the activity differences of bioactive molecules depending upon solvent type due to time/source restrictions. Herein, we show that theoretical analysis with DFT/TDDFT approaches could be a good alternative for determining the solvent effect. In this study, we analyzed the molecular orbital diagrams and electronic transitions of $[Mn(CO)_3(bpy)(L)]^+$ type complexes for various solvents.

Keywords: manganese carbonyl complexes; DFT/TDDFT; frontier orbital; electronic transitions

1. Introduction

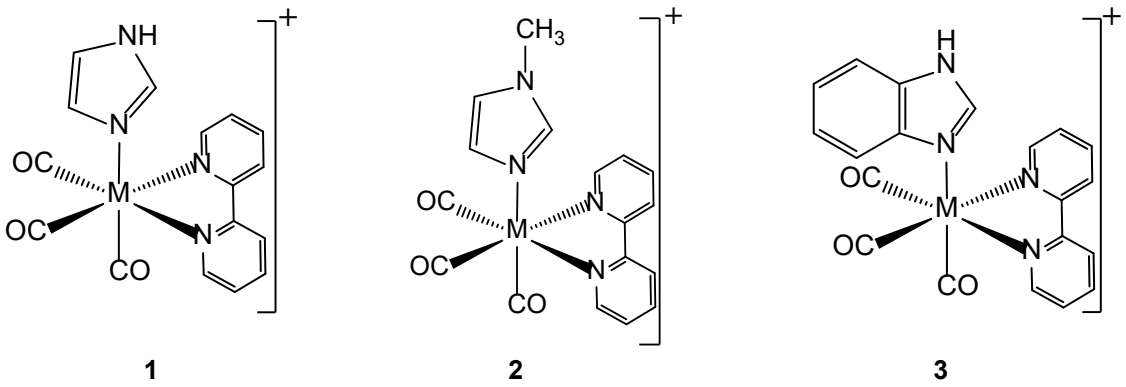
Metal carbonyl complexes have found wide use in industrial applications as catalysts after the first binary complex, $Ni(CO)_4$, was synthesized by Mond in 1890, although the first metal carbonyl complex, $[Pt(CO)Cl_2]_2$ was synthesized in 1868 [1]. Metal carbonyls have been also practiced in chemistry for many applications such as synthesis of complexes with photolysis [2], labeling of bioactive molecules [3], far-infrared studies in gas phase [4] and photosensitizers [5] owing to their unique photochemical and spectroscopic characteristics. Therefore, many metal carbonyl complexes have been analyzed for their bioactivities and revealed good results [6–10]. Recently, carbonyl complexes have attracted particular attention as good candidates for deposit and transport of carbon monoxide, which is accepted as a gasotransmitter [11–13].

Carbon monoxide (CO) is known as a poisonous gas. As the binding affinity of CO to hemoglobin is 240 times stronger than that of oxygen, excess production of carboxyhemoglobin impairs oxygen transport to tissues/organs and this is the primary reason of CO poisoning [14]. In fact, carboxyhemoglobin levels of up to 10% are asymptomatic and CO is endogenously produced in human body and has a beneficial and therapeutic effect [15]. In addition, experimental results show that exogenous supplements of CO could have therapeutic effects [12]. Because of this new finding, many molecules such as metal carbonyl complexes have been analyzed for their CO-releasing properties and many novel molecules have been synthesized/characterized as possible CO-releasing molecules (CORMs) [16–19]. Myoglobin assay is a well-known method for investigation of CO-releasing properties of the molecule [20]. In this method, chemically produced deoxymyoglobin interacts with CORMs in buffered solution to form carboxymyoglobin. Deoxymyoglobin/carboxymyoglobin

*Corresponding author. E-mail: elvanustun77@gmail.com, elvanustun@odu.edu.tr

transformation can easily be detected with a UV-Vis Spectrophotometer. The method shows similarity to many other in-vitro bioactivity measurement methods in terms of adding limited amount of sample, which is dissolved in convenient solvent, into the well-known standard measurement medium [17, 21–23]. However, Carrington et al. showed that the solvent type used in dissolution stage of myoglobin assay can change the numerical results of CO-releasing properties [24, 25]. It is also generally known that UV-Vis maxima of molecules depend on the solvent type [26]. Whereas, the main stages of in-vitro bioactivity trials should be independent from this kind of basic chemical factors for avoiding the troubles in possible in-vivo applications.

As a result of recent developments, DFT/TDDFT based calculation programs have been rendered as particularly useful tools for obtaining results compatible with the experimental data [27-30]. Moreover, these calculations avoid waste of time/source and make it possible to consider hypothetical approaches.



1 **2** **3**

Figure 1. Structures of *fac*-Manganese (I) tricarbonyl bipyridyl complexes with imidazole/benzimidazole ligands.

In this study, $[Mn(CO)_3(bpy)(L)]^+$ (bpy: 2,2-bipyridyl, L: imidazole, methylimidazole, benzimidazole) complexes that were synthesized/characterized previously (Fig. 1) [16] have been optimized in various solvents and TDDFT calculations were performed in four different solvents used in the synthesis and analysis procedures. Electronic transitions and structural parameters of the complexes have been evaluated depending upon solvent type. These calculations have given insight into the required features for a moderate bioactive species without any experimental procedure.

2. Results and Discussion

During in vitro bioactivity studies, generally a solution of the chemical sample is prepared with a convenient solvent and added to the standard measurement medium. It is well known that the dissolvent/total solution ratio is particularly important in standard activity measurement methods (such as antioxidant activity), especially in the case of buffered solution. For example, the CO-releasing rate of a manganese based carbonyl complex was 21.94 min^{-1} in dichloromethane but 11.22 min^{-1} in acetonitrile using the same measurement method under identical conditions [24, 25]. The discrepancy between the results is neither acceptable and nor suitable for possible in-vivo experiments. For this reason, type of the solvent has to be evaluated in this kind of measurements.

The activity differences depending upon solvent type of individual bioactive molecules cannot be analyzed because of the time and material restrictions. Alternatively, the chemical computational methods could be an ancillary way to investigate the solvent effect on the molecules. Developments in computational

chemistry have provided convenience to analyze structural parameters and spectroscopic characteristics of the molecules [27-33]. It is possible to search many different properties of organometallic complexes in not only gas phase but also in different solvents with the solvation models of program packages. In addition, some hypothetical conditions that are not experimentally possible could be considered. In this study, the molecules were optimized in several solvents that are used in synthesis and analysis procedures of molecules and the differences of structural parameters and electronic transitions were calculated. DFT/TDDFT calculations were carried out with ORCA version 2.8 [34-36]. BP86 functional [37, 38], which has been accepted slightly better than hybrid B3LYP functional in inorganic compounds [39], was used in the calculations with the resolution-of-the-identity (RI) approximation for speedup the calculations [40]. A def2-TZVP/def2-TZVP/J basis set, the tightscf and grid4 options, and the COSMO solvation model [41, 42] that is frequently used computationally efficient continuum dielectric approach [43,44], were also utilized.

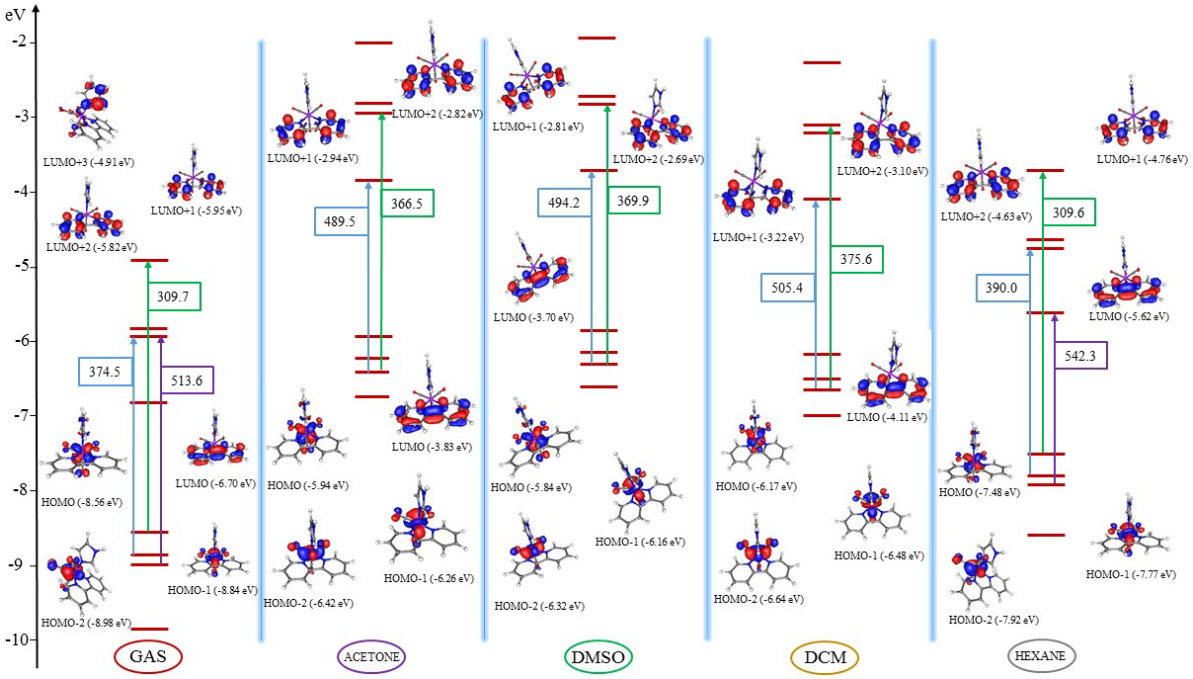


Figure 2. Frontier orbital plots, energies of frontier orbitals and considerable electronic transitions of **1** in different solvents. (The representing unit of electronic transition energy values are given in nm).

Molecular orbital energy diagrams of the molecules in gas form have been drawn and given in Fig. S1. The molecular orbital energies of **1** have exemplarily been analyzed (Fig. 2). **1** has the lowest molecular orbital energies in gas form. The highest molecular orbital energies of **1** occurred in the calculations with polar solvents. The calculated energies in hexane are lower than that of polar solvents but slightly higher than gas phase. HOMO energy in gas phase is -8.56 eV while -7.58 eV is calculated in hexane. In acetone and dichloromethane (DCM) that were used in synthetic procedure of the molecules and in dimethylsulfoxide (DMSO) which was used for analyzing the CO-releasing properties, the HOMO energies of the molecules have been determined -5.94 eV, -6.17 eV and -5.84 eV, respectively. The most prominent electronic transitions of the molecule according to oscillator strength in gas phase, acetone, DMSO, dichloromethane and hexane have been evaluated in Fig. 2. If the calculation results of the molecules that studied in this study were evaluated, the electronic transitions with the oscillator strength higher than 0.04 have been appreciated as a distinguishable transition, which could be observed in UV-Vis spectroscopy (Figure S2) [45, 46]. Three electronic transitions in gas phase and hexane and two electronic transition in polar solvents have been recorded

with different wavelengths. The additional HOMO→LUMO+3 transition in gas and hexane at 310 nm have notable oscillator strength unlike the polar solvents. The transitions with maximum oscillator strength have been calculated as 374.5 nm in gas phase, 390.0 nm in hexane, 366.5 nm in acetone, 369.9 nm in DCM and 375.6 nm in DMSO.

It is well known that the energy gap between HOMO and LUMO molecular orbitals is a good indication for the (re)activity of the molecules [47]. HOMO energy of a molecule is an evidence of ionization potential while LUMO energy of a molecule is relevant to electron affinity. In addition, chemical potential and electrophilicity index could be evaluated by HOMO and LUMO energies of the molecules [48, 49]. Therefore, the molecules with large HOMO-LUMO gap have been defined hard molecules while the molecules with small HOMO-LUMO gap have been defined soft molecules and the hardness/softness is used as a measure of kinetic stability. The soft molecules are more reactive than the hard molecules if a reaction includes electron transfer or rearrangement [50]. The changes of HOMO-LUMO energy gap of **2** occurring on solvent differences have been illustrated in Fig. 3. The HOMO-LUMO energies are greater in polar solvents relative to that in hexane and gas phase. It is means that the solution of **2** in DMSO is more stable to the electron transfer or rearrangement.

The electronic transitions of optimized **3** have also been evaluated in different solvents and generally labelled as MLCT (metal to ligand charge transfer). In gas phase, among the eight prominent electronic transitions, the transition with the highest intensity has been calculated in 390.3 nm as a MLCT (Table S1). Three MLCT calculated from HOMO, HOMO-1 and HOMO-2 to LUMO have longer wavelength with respect to others. The only ligand to ligand charge transfer (LLCT) was consisted of HOMO-4 → LUMO+1 with 0.0351 oscillator strength in 343.3 nm as the 15th state in gas phase. The electronic transitions in acetone, DCM, DMSO and hexane are presented in Tables S2-S5.

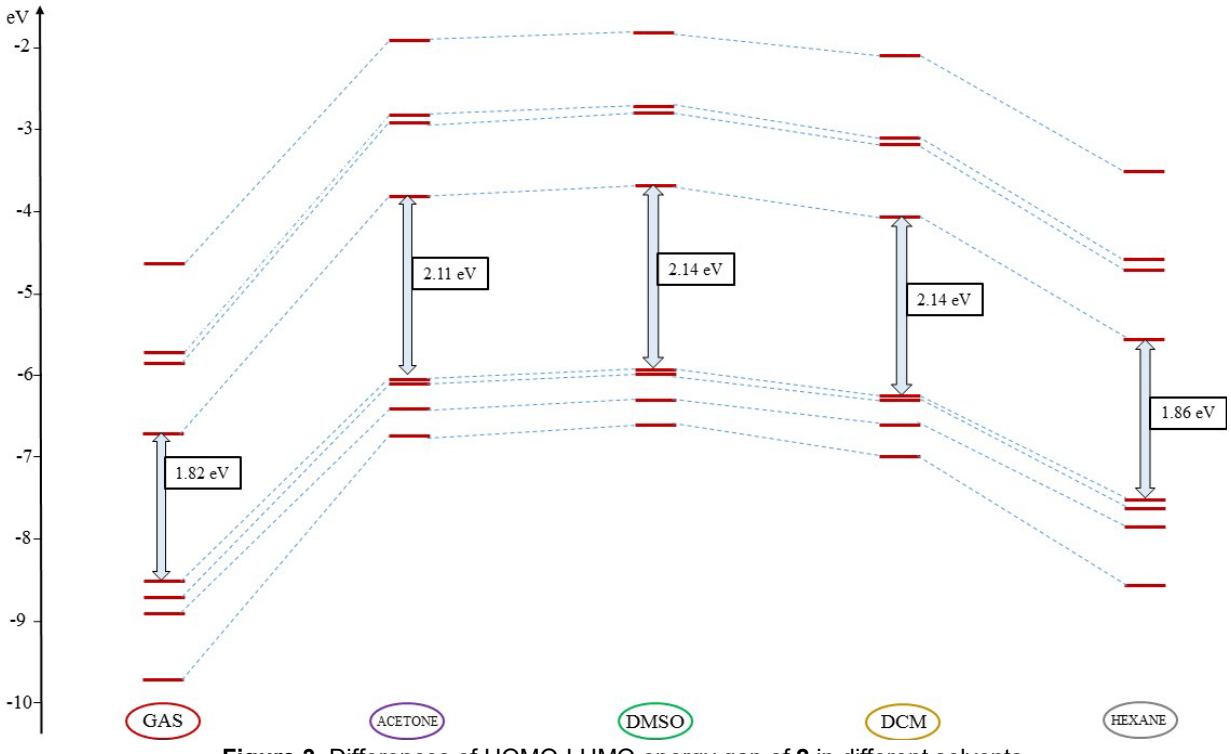


Figure 3. Differences of HOMO-LUMO energy gap of **2** in different solvents.

The determined bond lengths and angles of the molecules in various solvents have been evaluated in Table S6. In polar solvents, M-CO bond lengths of the molecules have shortened when the C-O bond lengths have elongated. M-CO and C-O bond lengths of **3** are not considerably affected by solvent type and this could be attributed to the relatively higher

conjugation of the ligand. In addition, significant differences in the bond angles of the molecules could not be calculated.

Conclusions

The solvent effect on the electronic transitions of $[Mn(CO)_3(bpy)(L)]^+$ (bpy: 2,2-bipyridyl, L: imidazole, methylimidazole, benzimidazole) complexes have been evaluated theoretically by DFT/TDDFT based ORCA package program. Bioactivity analyses generally require dissolution of solid organometallic molecules in an appropriate solvent. The electronic character as well as the bioactivity properties of organometallic complexes change when different solvents are considered. It is essential for the solvents, which are generally chosen depending on their solving capabilities, to be suitable for actual medicinal implementations and be preferably biocompatible. Since MLCT and LLCT characters of compounds are affected by solvents, the bioactivity measurement procedures, especially the ones that use a light source such as Myoglobin-Assay, must be considered with regard to solvent type.

Acknowledgements

The Scientific and Technological Research Council of Turkey (TÜBİTAK) under Grant 112T320 supported this work.

References and Notes

[1] Mond, L.; Langer, C.; Quincke, F. *J. Chem. Soc. Trans*. **1890,** *57*, 749. [Crossref]

[2] Szymańska-Buzar, T.; Kern, K.; Downs, A. J.; Greene, T. M.; Morris, L. J.; Parsons, S. *New J. Chem.* **1999**, *23*, 407. [Crossref]

[3] Mokhtari, M.; Mousser, A.; Salmain, M.; Jaouen, G. *Comptes Rendus Chimie* **2005,** *8*, 85. [Crossref]

[4] Bencze, É.; Mink, J.; Pápai, I.; Butler, I. *J. Organomet. Chem.* **2000**, *616*, 1. [Link]

[5] Wähler, K.; Ludewig, A.; Szabo, P.; Harms, K.; Meggers, E. *Eur. J. Inorg. Chem.* **2014**, 807. [Crossref]

[6] Hillard, E. A.; Jaouen, G. *Organometallics* **2011**, *30*, 20. [Crossref]

[7] Navarro, M.; Castro, W.; Biot, C. *Organometallics* **2012**, *31*, 5715. [Crossref]

[8] Noffke, A. L.; Habtemariam, A.; Pizarro, A. M.; Sadler, P. J. *Chem. Commun*. **2012**, *48*, 5219. [Crossref]

[9] Hartinger, C. G.; Dyson, P. J. *Chem. Soc. Rev.* **2009**, *38*, 391. [Crossref]

[10] Meister, K.; Niesel, J.; Schatzschneider, U.; Metzler-Nolte, N.; Schmidt, D. A.; Havenith, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 3310. [Crossref]

[11] Johnson, T. R.; Mann, B. E.; Teasdale, I. P.; Adams, H.; Foresti, R.; Green, C. J.; Motterlini, R. *Dalton Trans.* **2007**, 1500. [Crossref]

[12] Motterlini, R.; Otterbein, L. E. *Nat. Rev. Drug Discovery* **2010**, 728. [Crossref]

[13] Foresti, R.; Bani-Hani, M. G.; Motterlini, R. *Intensive Care Med.* **2008**, *34*, 649. [Crossref]

[14] Hanafy, K. A.; Oh, J.; Otterbein, L. E. *Curr. Pharm. Des.* **2013**, *19*, 2771. [Crossref]

[15] Romão, C. C.; Blättler, W. A.; Seixas, J. D.; Bernardes, G. J. L. *Chem. Soc. Rev.* **2012**, *41*, 3571. [Crossref]

[16] Üstün, E.; Özgür, A.; Coşkun, K. A.; Demir, S.; Özdemir, İ.; Tutar, Y. *J. Coord. Chem.* **2016**, *69*, 3384. [Crossref]

[17] Nobre, L. S.; Seixas, J. D.; Romão, C. C.; Saraiva, L. M. *Antimicrob. Agents Chemother.* **2007**, *51*, 4303. [Crossref]

[18] Davidge, K. S.; Sanguinetti, G.; Yee, C. H.; Cox, A. G.; McLeod, C. W.; Monk, C. E.; Poole, R. K. *J. Biol. Chem.* **2009**, *284*, 4516. [Crossref]

[19] Motterlini, R.; Haas, B.; Foresti, R. *Med. Gas Res.* **2012**, *2*, 28. [Crossref]

[20] Johnson, T. R.; Mann, B. E.; Clark, J. E.; Foresti, R.; Green, C. J.; Motterlini, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 3722. [Crossref]

[21] Biot, C.; Glorian, G.; Maciejewski, L. A.; Brocard, J. S.; Domarle, O.; Blampain, G.; Lebibi, J. *J. Med. Chem.* **1997**, *40*, 3715. [Crossref]

[22] Lemke, J.; Pinto, A.; Niehoff, P.; Vasylyeva, V.; Metzler-Nolte, N. *Dalton Trans.* **2009**, 7063. [Crossref]

[23] Üstün, E.; Çol Ayvaz, M.; Sönmez Çelebi, M.; Aşci, G.; Demir, S.; Özdemir, İ. *Inorg. Chim. Acta* **2016**, *450*, 182. [Crossref]

[24] Carrington, S. J.; Chakraborty, I.; Alvarado, J. R.; Mascharak, P. K. *Inorg. Chim. Acta* **2013**, *407*, 121. [Crossref]

[25] Carrington, S. J.; Chakraborty, I.; Mascharak, P. K. *Chem. Comm.* **2013**, *49*, 11254. [Crossref]

[26] Chagas, M. A.; Rocha, W. R. *Chem. Phys. Lett.* **2014**, *612*, 78. [Crossref]

[27] Makedonas, C.; Mitsopoulou, C. A. *Inorg. Chim. Acta* **2007**, *360*, 3997. [Crossref]

[28] Pai, S.; Hafftlang, M.; Atongo, G.; Nagel, C.; Niesel, J.; Botov, S.; Schmalz, H. G.; Yard, B.; Schatzschneider, U. *Dalton Trans.* **2014**, *43*, 8664. [Crossref]

[29] Chakraborty, I.; Carrington, S. J.; Mascharak, P. K. *Acc. Chem. Res.* **2014**, *47*, 2603. [Crossref]

[30] Xue, Z.; Wang, Y.; Mack, J.; Zhu, W.; Ou, Z. *Chem. - Eur. J.* **2015**, *21*, 2045. [Crossref]

[31] Wick, C. R.; Smith, D. M. *J. Phys. Chem. A* **2018**, *122*, 1747. [Crossref]

[32] Aoto, Y. A.; Batista, A. P. L.; Köhn, A.; Filho, A. G. S. O. *J. Chem. Theory Comput.* **2017**, *13*, 5291. [Crossref]

[33] Brandenburg, J. G.; Bannwarth, C.; Hansen, A.; Grimme, S. *J. Chem. Phys.* **2018**, *148*, 064104. [Crossref]

[34] Pantazis, D. A.; Chen, X. Y.; Landis, C. R.; Neese, F. *J. Chem. Theory Comput.* **2008**, *4*, 908. [Crossref]

[35] Neese, F. *WIREs Comput. Mol. Sci.* **2012**, *2*, 73. [Crossref]

[36] Neese, F. *Coord. Chem. Rev.* **2009**, *253*, 526. [Crossref]

[37] Perdew, J. P. *Phys. Rev. B Condens. Matter.* **1986**, *33*, 8822. [Crossref]

[38] Becke, A. D. *Phys. Rev. A* **1988**, *28*, 3098. [Crossref]

[39] Neese, F. *J. Biol. Inorg. Chem.* **2006**, *11*, 702. [Crossref]

[40] Neese, F. *J. Comput. Chem.* **2003**, *24*, 1740. [Crossref]

[41] Klamt, A.; Schüürmann G. *J. Chem. Soc. Perkin Trans.* **1993**, *2*, 799. [Crossref]

[42] Sinnecker, S.; Rajendran, A.; Klamt, A.; Diedenhofen, M.; Neese, F. *J. Phys. Chem. A* **2006**, *110*, 2235. [Crossref]

[43] Franco, J. M. V.; Schnakenburg, G.; Sasamori, T.; Ferao, A. E.; Streubel, R. *Chem. - Eur. J.* **2015**, *21*, 9650. [Crossref]

[44] Schulz, H.; Görling, A.; Hieringer, W. *Inorg. Chem.* **2013**, *52*, 4786. [Crossref]

[45] Salassa, L.; Garino C.; Salassa, G.; Gobetto, R.; Nervi, C. *J. Am. Chem. Soc.* **2008**, *130*, 9590.[Crossref]

[46] Hartl, F.; Rosa, P.; Ricard, L.; Le Floch, P.; Zȧlis, S. *Coord. Chem. Rev.* **2007**, *251*, 557. [Crossref]

[47] Geerlings, P.; De Proft, F.; Langenaeker, W. *Chem. Rev.* **2003**, *103*, 1793. [Crossref]

[48] Pearson, R. G. *Proc. Nati. Acad. Sci. USA* **1986**, *83*, 8440. [Crossref]

[49] Aihara, J. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3121. [Crossref]

[50] Chen, H.; Delaunay, W.; Yu, L.; Joly, D.; Wang, Z.; Li, J.; Wang, Z.; Lescop, C.; Tondelier, D.; Geffroy, B.; Duan, Z.; Hissler, M.; Mathey, F.; Reau, R. *Angew. Chem. Int. Ed.* **2012**, *51*, 214. [Crossref]