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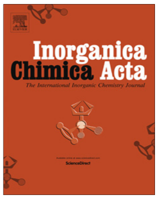

Research paper

Iron phenanthrolines: A density functional theory study

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ABSTRACT

A comprehensive DFT study on the most extensive series of 1,10-phenanthroline iron complexes, to date, is reported here. Results have relevance to fields of active research; amongst others that of metal-to-ligand charge transfer complexes and of redox indicators. ADF geometry optimizations at the BP86/TZP level for a series of twenty-four iron complexes with substituted phenanthrolines for which electrochemical data is available, were obtained. Visible light excitations in these MLCT complexes involve transitions from the upper three metal based HOMO's to the lower five ligand based LUMO's. With high accuracy calculated HOMO energies, ionization potentials and Mulliken electronegativities are linearly correlated with experimentally obtained redox data from different studies. Molecular orbital renderings and TDDFT computed oscillators are illustrated to closely predict and explain experimental data. As part of the establishment of a larger data base, also for iron phenanthrolines an experimentally vindicated basis is now presented by which its chemical properties may theoretically be ascertained before embarking on more demanding experimental procedures.

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1. Introduction

Synthesis of 1,10-phenanthrolines was reported as far back as 1930, where Smith used the Skraup reaction to produce phenylenediamines, which in turn were converted to phenanthrolines [1]. Oxidation of phenanthroline yields dipyridyl dicarboxylic acid, and eventually dipyridyl – after decomposition of the acid substituents while heating. Together with terpyridyl, all these compounds represent a group of aromatic nitrogen heterocycles that readily complexes transition metals. The ligand N σ-donor ability however is poor, but this is compensated for by these ligands' ability to be good π-acceptors [2]. Low energy $\pi*$ orbitals give rise to strong visible spectrum metal-to-ligand charge transfer absorption bands and red-shifted fluorescence in its metal complexes. Therefore, as pointed out by Bencini and Lippolis in an extensive recent review article [3], these ligands are often employed during pH and energy transfer studies – particularly in dye-sensitized solar cells, but also in catalyses, materials and biochemistry.

The *tris*-coordinated iron phenanthroline complex, otherwise known as ferroin, is probably the most well studied complex in this group, especially with regard to its function as redox indicator during photometric determinations of the divalent iron cation. Skoog and West note that "of all the oxidation/reduction indicators, ferroin approaches most closely the ideal substance. It reacts rapidly and reversibly, its colour change is pronounced, and its solutions are stable and easily prepared" [4]. The oxidized [Fe(phen)$_3$]$^{3+}$ species is light blue, while the reduced [Fe(phen)$_3$]$^{2+}$ complex has a deep red colour. Electron withdrawing and/or donating groups substituted on the heterocyclic ring is conveniently used to tune electrochemical and spectral properties of the ligand and its complexes. Hereby the colour/redox transition potentials in aqueous 1 M H_2SO_4 are 1.25 V for the 5-NO_2 derivative, 1.11 V for unsubstituted phenanthroline and 1.02 V for the 5-CH_3 species (see substituent position numbering in Fig. 1). A recent study reported redox data for a wide range of electrochemically altered derivatives, albeit in organic (CH_3CN) medium [5]. Whereas the formal reduction potential ($E^{0\prime}$) of the 5-NO_2 [Fe(phen)$_3$]$^{3+}$ complex was observed at 0.894 V, $E^{0\prime}$ for the 5-CH_3 analogue lies at 0.669 V. Regardless differences in media and electrode systems resulting in recorded potentials in the organic solvent being lower, the potential difference between the 5-NO_2 and 5-CH_3 species are nevertheless strikingly similar; in both 1 M H_2SO_4 and CH_3CN media being 0.23 V. Additionally, $E^{0\prime}$ for unsubstituted terpyridyl, phenanthroline and bipyridyl complexes lie closely grouped together, within 0.038 V from each other [5]. The substituents on the aromatic pyridyl rings therefore have a larger influence on the redox potential of the complex metal than the composition of the ring system, whether phenanthroline, bipyridine or terpyridine.

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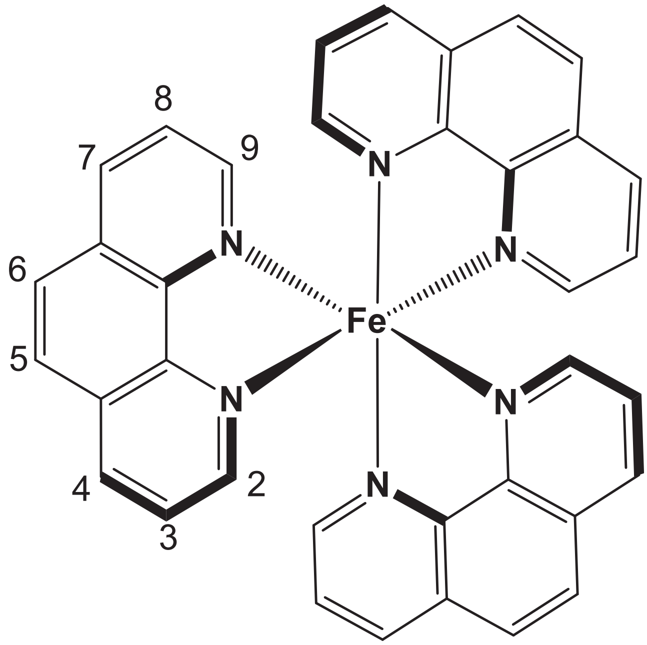

Fig. 1. Fe(phen)$_3$ structure, with ligand substitution numbering scheme indicated.

As opposed to the highest occupied molecular orbital (HOMO) which is localized on the central metal, the lowest unoccupied molecular orbital (LUMO) is delocalized over all three ligands [5]. During oxidation of $[Fe(phen)_3]^{2+}$ an electron is removed from the metal-based HOMO of the complex. Partially related is the electron density that gets transferred from the metal-based HOMO to the ligand-based LUMO during photochemical excitation (*ca* 510 nm) [5]. This characteristic results in these iron complexes being categorized as metal-to-ligand charge transfer complexes (MLCT). Low-lying $\pi*$ orbitals, as often seen in aromatic ligands, are commonly associated with these complexes. With the metal being at lower oxidation state, transitions occur at sufficiently low energies to fall within the visible part of the spectrum and thus overlapping with the section of the solar spectrum where maximum irradiation is measured. This is particularly true for the favoured ruthenium bipyridyl and terpyridyl solar cell dyes [6,7].

Applied research in the latter field often requires the gathering of huge amounts of experimental data. With the advent of modern quantum computational capabilities this may however be fast-tracked by theoretical simulations. Up to date only limited comprehensive studies had however seen the light, especially due to the large size and consequent expense in computational time required for the molecules here under consideration. The widest range of cyclic voltammetry data obtained from literature was consequently extracted and compared to computed energies and related descriptors, employing density functional theory with the BP86 functional as part of the ADF software package. A series of twenty-four $[Fe(phen)_3]^{2+}$ complexes with various substituents on the phenanthroline ligands and for which cyclic voltammetry are available were geometry optimized, molecular orbital renderings obtained and TDDFT electronic oscillators calculated.

Finding best correlations between quantum computational descriptors and electrochemical data had for some time been one objective of our research [8–12]. The most significant outcome has been the very close linear correlations found between computed energies of series of systematically modified compounds and their experimental reduction or oxidation peak potentials. Having started with simple electrochemically well-behaved nitrobenzenes [13], the study advanced to bidentate ligands [14,15], and single as well as bimetallic complexes [16], where the latter reference also gives a brief review of the very limited reports in this field. At about the same time Lever did an extensive computational study of series of Ru complexes [17]. The NPA and total Mulliken charge on non-innocent ligands in these complexes were correlated with reduction potentials of the Ru complexes. The use of experimental data from a variety of laboratories and the use of different electrodes was presented as reason for the less than optimal scatter seen in correlation graphs. However, the Mulliken charges gave neat linear relationships, as did E_{LUMO}, when homologous series of complexes were involved [18]. Calculated Gibbs free energy is yet another quantity *via* which experimental redox data may closely be correlated [19].

In 1933 Koopman's theorem pointed to the direct relationship between ionization energy and the HOMO energy of a molecule [20]. Consequently oxidation potentials would relate to HOMO energies, while LUMO energies relate to reduction potentials. In 2006 Sereda et al. remarked about the convenience of Koopman's theorem which allows ignoring solvation of the open shell reduced species, while only characterizing the starting compound [21].

2. Theoretical approach

Density functional theory (DFT) calculations were performed using the GGA functional BP86 [22,23] with the TZP (Triple ζ polarized) basis set as implemented in the Amsterdam Density Functional (ADF2013 and updates) [24] as well as the B3LYP hybrid functional [25,26] with the triple-ζ basis set 6-311G basis set as implemented in Gaussian 09 [27]. All complexes were computed in the gas phase and spin unrestricted, spin S = 0 for Fe(II), and S = ½ for Fe(I) (reduced) and Fe(III) (oxidized). Frequency analysis did not give any imaginary frequencies, i.e. true minima. Selected DFT calculated energies and thermodynamic data are given in the Table 2. TD-DFT calculations were done with spin restricted and spin unrestricted TD-BP86 for Fe(II) and Fe(III) respectively, calculating the lowest energy 300 excitations. Geometry relaxed (adiabatic) energies of the complexes (*N* electron system), and the corresponding N − 1 (reduced) and N + 1 (oxidized) electron systems were calculated to determine electron affinity (EA), ionization potential (IP) and Mulliken electronegativity (χ), by application of the following formulas [28,29].

$$\mathrm{EA(complex)} = E(\text{reduced complex}) - E(\text{complex})$$
$$\mathrm{IP(complex)} = E(\text{oxidized complex}) - E(\text{complex})$$
$$\chi = (\mathrm{IP} + \mathrm{EA})/2$$

3. Results and discussion

The X-ray crystal structure of the $[Fe(phen)_3]^{2+}$ complex deviates only slightly from a perfect octahedral geometry. Smallest angles of less than 90°, varying from 82.1 to 83.8°, are associated with the dative covalent bonds that the two nitrogens of any single ligand form with the central metal [30]. Consequently bond angles between adjacent ligands are 90° or larger. Similar results are found in theoretically calculated structures of this study, where again, the angles formed by the bidentate bonds are 82.5°. In certain X-ray crystal structures bond angle and length variations do occur, but this is attributed to crystal packing affects.

From about 150 available crystal structures (*Cambridge Crystallographic Database* [31]) experimental Fe—N bond distances in $[Fe(phen)_3]^{2+}$ complexes average at 1.976 Å. C—N bonds within one particular ligand in a complex varies from 1.332 to 1.369 and C—C bonds from 1.351 to 1.436 Å [30], see Table 1. These bond distances are representative of all phenanthroline ligands. Comparison with corresponding theoretically computed bond lengths show close agreement, namely 1.983, 1.344–1.372, and 1.385–1.436 Å. As for the oxidized $[Fe(phen)_3]^{3+}$ complexes, X-ray data

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