Metal–ligand interactions in Fe(II)-dioxime complexes

Balázs Krámos [a], Attila Kovács [b],*

[a] Faculty of Bio- and Chemical Engineering, Budapest University of Technology and Economics, H-1111 Budapest, Szt. Gellért tér 4, Hungary
[b] Materials Structure and Modeling Research Group of the Hungarian Academy of Sciences, Budapest University of Technology and Economics, H-1111 Budapest, Szt. Gellért tér 4, Hungary

ARTICLE INFO

ABSTRACT

The structural and bonding characteristics of Fe(II)-dioxime complexes of the type $[Fe(dmgH)_2L_2]$ (where $dmgH_2$ = dimethylglyoxime; L = 2-NH$_2$-tiazole, pyridine, 4-methylpyridine, diethyl(phenyl)phosphine, diethyl(p-tolyl)phosphine) and $[Fe(diox)_3B(OR')_2]$ (where diox = dmg, cyclohexanedione dioximate; R' = H, CH$_3$, propyl) were investigated by means of quantum chemical computations. The equilibrium geometries and bonding properties were computed using the B3LYP exchange-correlation density functional in conjunction with a relativistic effective core potential and a polarized valence basis set for Fe, while 6-311G** basis sets for the other atoms. The characteristics of the metal–ligand interactions were elucidated by natural bond orbital analysis.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Dioxime (dioxH$_2$) ligands are known about their important role in analytical chemistry. They form stoichiometric complexes with several metals, the precipitate complexes being well suited for the gravimetric determination of these metals [1,2]. Spectrophotometric determination is also often possible when the precipitate can be dissolved in an appropriate solvent [3]. The general characteristics of the structure of transition metal dioxime complexes are summarised in the early review of Chakravorty [4].

The above application is based on the strong bonding interactions in the complexes. Beside the strong metal–ligand bonds the $[M(dioxH)_2L_x]$ (x = 0–2) complexes are characterised by very strong O...H–O hydrogen bonds between the symmetrically arranged anionic oximate ligands. The nature of these bonding interactions has been revealed in our recent study of $[M(dmgH)_2]$ (M = Ni, Pd, Pt; dmgH$_2$ = dimethylglyoxime) [5]. We showed that without the metal ion between the ligands the hydrogen bonds are much weaker. The strong metal–ligand bonds pull the dimethylglioximate ligands together, while the metal–ligand bond strength showed a reversed relation with the size of the metal ion.

The analogous dioxime complexes of Fe(II), Fe(dioxH)$_2$, are less stable, they are, e.g., easily soluble in water. They can be stabilized by two additional ligands in the axial position (Scheme 1a), gener-

ally by amines, phosphines or N-heterocycles [6], in this form already suited for qualitative micro-analytical determination of Fe(II).

The hexacoordination of Fe(II) is achieved also in clathrochelate-type complexes, where three dioximes surround the central metal. In such complexes the dioximes are additionally fixed by apical BOR' groups (Scheme 1b). These compounds are suitable models for electron transfer in biological systems and can be used as catalysts of redox reactions [7,8].

In this paper we report a comparative analysis of the bonding in the above two types of Fe(II)-dioxime complexes by means of DFT quantum chemical calculations. The selected model compounds using various ligands are summarised in Scheme 1 including also the numbering of complexes used in further parts of the paper. Beside the structural characteristics we focus on the metal–ligand interactions. A quantitative assessment of the latter interactions is performed by natural bond orbital (NBO) [9] analysis. To the best of our knowledge the only theoretical study of Fe(II)-dioxime complexes hitherto is the DFT investigation of the structure and vibrational frequencies of $[Fe(methylglyoxime)_2(pyridine)_2]$ [10].

2. Computational details

The computations were performed using the B3LYP exchange-correlation functional [11,12] in conjunction with the effective core potential of Hay and Wadt for Fe [13], its valence basis set extended by 2fg polarization functions (the exponents were 3.516, 0.871 and 2.269, respectively) and the 6-311G** basis set for the other elements. The characters of the stationary points were

* Corresponding author. Address: Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, H-1111 Budapest, Szt. Gellért tér 4, Hungary. Tel.: +36 1 463 2278; fax: +36 1 4633408.
E-mail address: akovacs@mail.bme.hu (A. Kovács).
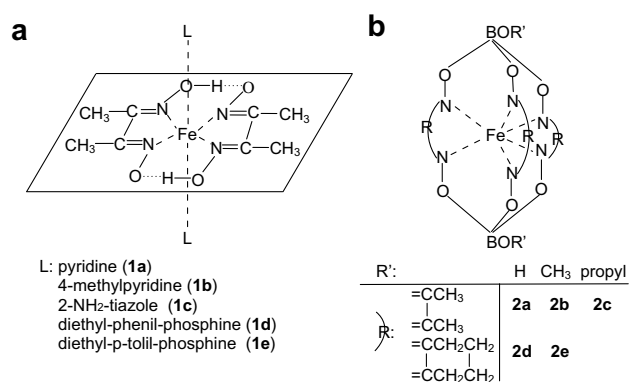
Scheme 1.
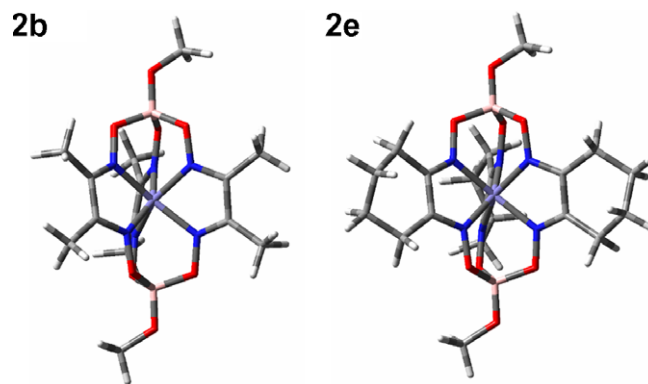
Fig. 2. Optimized structures of the clathrochelate complexes **2b** and **2e**.

always checked by frequency analyses. The electronic ground state of the complexes was verified by test calculations on **1a** and **2a**. These results indicated the singlet character of the ground state in each case, the triplet states lying higher over 50 kJ/mol, while the quintet ones over 80 kJ/mol.

The calculations were carried out with the Gaussian 03 [14] program package. The natural bond orbital analyses [9] were performed using the NBO 5.0 code [15]. The computed structures were visually analysed by the GaussView 4.1.2 program [16].

3. Results and discussion

3.1. Molecular geometries

As can be recognised from Scheme 1, the skeleton of the complexes is rather rigid. Conformational variations can appear in the relative orientations of L and R′ in complexes **1** and **2**, respectively, in the orientations of the ethyl groups in the phosphine ligands in **1d** and **1e** as well as in the conformation of the cyclohexane ring in **2d** and **2e**. We investigated the possible conformations of all complexes included in this study.

In **1a** and **1b** only one orientation is possible for pyridine and 4-methylpyridine, respectively. Both ligands are connected to Fe by the ring N atom, the plane of the aromatic rings being perpendicular to the plane of the bis(dimethylglyoximato)Fe(II) moiety (cf. Fig. 1). The aromatic ring is oriented in a way that the two ortho hydrogens establish weak bifurcated O...(C)H...N hydrogen bonding interactions with the deprotonated N–O moieties of dimethylglyoxime (H...O = 2.36 Å, H...N = 2.47 Å in both complexes). These weak interactions provide minor contributions to the stabilization of the complexes.

In **1c** the tiazole ligand can coordinate to Fe by the ring N and S atoms. The former case was found to be the global minimum on the potential energy surface, while the S-coordinated complex is a local minimum lying higher by 121 kJ/mol. In the global mini-

mum structure (cf. Fig. 1) the arrangement of the tiazole ligand is similar to those of pyridine and 4-methylpyridine: one of the NH_2 hydrogens forms bifurcated hydrogen bond with a deprotonated N–O moiety (H...O = 1.79 Å, H...N = 2.24 Å), while the ring hydrogen ortho to the ring N forms weak hydrogen bonds with the deprotonated N–O moiety of the other dmgH (H...O = 2.35 Å, H...N = 2.50 Å).

The phosphine ligands in **1d** and **1e** can form several conformers depending on the relative orientations of the two ligands as well as on the rotation of their phenyl, tolyl and ethyl groups. The local minima were found to be less stable by 8–10 kJ/mol. The structure of the global minimum of **1d** (analogous to **1e**) is shown in Fig. 1. In this structure the hydrogens of a phosphine ligand establish five weak hydrogen bonds with N–O and N–OH moieties of dmgH (with distances $H_{Ph}...O = 2.19$ Å, $H_{Ph}...N = 2.44$ Å, $H_{Et1}...OH = 2.40$ Å, $H_{Et1}...O = 2.44$ Å, $H_{Et2}...OH = 2.31$ Å).

In the chlatrochelate complexes (Fig. 2) the main conformational variations are manifested in the synperiplanar or anticlinal relative orientations of the two R′ substituents. With R′ = H the anticlinal, while with R′ = CH_3 and propyl the synperiplanar conformers proved to be the global minima on the potential energy surface, but the energy differences were small (below 0.6 kJ/mol). In addition, the envelope conformation of the cyclohexane rings can flip in **2d–e** resulting in energy changes of around 1 kJ/mol. Due to the compact structure of the ligand, there are no hydrogen bonds in complexes **2**.

Selected geometrical parameters are depicted in Table 1. The most interesting parameters in the studied complexes are the Fe–N bonds being characteristic on the metal–ligand interactions. The Fe–N(O) and Fe–N(OH) bond distances are only slightly different in complexes **1a–e** indicating that the protonated/deprotonated character of N has a marginal effect on the Fe–N interaction. The distances of the axial N-heterocyclic ligands from Fe are larger by 0.11–0.15 Å, implying a weaker character of their bonding. The effect of the methyl group in the pyridine/toluene pairs (**1a–b** and **1d–e**) is marginal on the coordination bonds. On the other hand, the character of the L ligand (pyridine, tiazole, phosphine) influences considerably the strong hydrogen bond between the dimethylglioximate moieties. It is the weakest in **1c**, where the strong hydrogen bond with the NH_2 group (vide supra) reduces the proton acceptor ability of the deprotonated oxygen towards NOH of the other dmgH moiety. The strongest character of the (O)H...O hydrogen bonds in **1d–e** may be attributed to the large number of weak hydrogen bonds between the phosphine ligand and the N–O...H–O–N moiety, where the weak hydrogen bonds polarize also the OH oxygen increasing its proton donor ability. The O...H distances of 1.6–1.7 Å in **1a–e** are longer by ca. 0.2 Å than the hydrogen bond in [Ni(dmgH)_2] while agree with the O...H distances found in [Pd(dmgH)_2] and [Pt(dmgH)_2] [5].
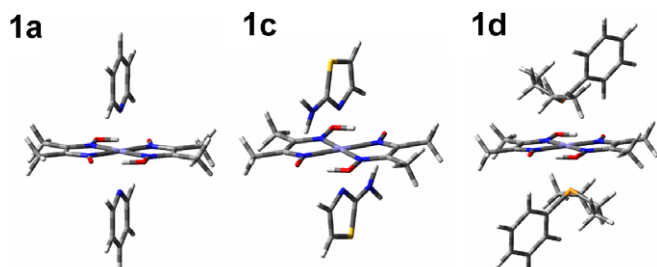
Fig. 1. Optimized structures of the complexes **1a**, **1c** and **1d**.