



Structural description relying on characteristic spectral data for a series of iron complexes having Schiff bases as anionic bidentate ligands

Research article

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Abstract

The purpose of this work is giving a structural description - based on the interpretation of the characteristic spectral data - for a series of six new Fe(II) complexes that contain triphenylphosphine/triphenylarsine and Schiff bases obtained by condensation of hydroxynaphthaldehyde with primary aromatic amines as bidentate ligands, namely 1-((phenylimino)methyl)naphthalen-2-ol, 1-((*p*-chlorophenylimino)methyl)naphthalen-2-ol and 1-((*o*-tolylimino)methyl)naphthalen-2-ol, which are denoted as LH, L'H and L''H respectively (because each of them is going to lose a hydrogen atom during coordination to the central ion, so as the remaining parts of the molecule could be denoted as L, L' and L''). Beside the elemental analysis, the molar conductivity and also magnetic susceptibility measurements, IR, ¹H-NMR and electronic spectra have been performed in order to investigate if the Schiff bases really act as uninegative bidentate ligands (all of them are diamagnetic, showing the (+2) oxidation state of iron). Indeed, by gathering all the results, a "trans" octahedral structure has been proved for all the six investigated complexes.

Keywords: complex compounds, iron ion, Schiff bases, bidentate ligands, spectral analysis

1. INTRODUCTION

As a part of the investigations on the reactions of Fe(II) complexes with Schiff base ligands, we will herein report the synthesis and the characterization of a series of six iron complexes with the following three ligands: LH = 1-((phenylimino)methyl)naphthalen-2-ol, L'H = 1-((*p*-chlorophenylimino)methyl)naphthalen-2-ol and also finally L''H = 1-((*o*-tholylimino)methyl)naphthalen-2-ol, also containing triphenylphosphine or triphenylarsine. The compounds formed by Fe(II) with these Schiff bases will be proved to be hexa-coordinate, exhibiting an octahedral geometry [1, 2].

2. EXPERIMENTAL

2.1. Preparation method

Preparation of the complex compounds of Fe(II) with the Schiff bases was carried out as follows: two complexes, $[\text{FeHCl}(\text{CO})(\text{PPh}_3)_3]$ and $[\text{FeHCl}(\text{CO})(\text{AsPh}_3)_3]$ all the ligands were prepared according to the literature procedures.

Then, each Schiff base was added in a 1:1 molar ratio to a solution of $[\text{FeHCl}(\text{CO})(\text{EPh}_3)_3]$ (0.1 g; 0.07 - 0.1 mmol) in benzene (20 cm³), where E stands for either P or As.

The mixture was boiled under reflux for six hours; the resulting solution was concentrated to 3 cm³ and the product was separated by addition of a small amount of light petroleum (at 70 °C). It was filtered and recrystallized from light petroleum and then dried under vacuum.

All the reagents used were of A.R. grade.

2.2. Instruments

The elemental analysis was performed on a Perkin Elmer 2380 analyzer.

The molar conductivities were determined in DMF by using an OK-102 conductivity-meter at 25 °C. The magnetic susceptibility measurements were performed on a Gouy balance, at 25 °C as well.

The ¹H-NMR data were obtained on a Varian Gemini 300 BB (at 300 MHz) using DMF as a solvent. The IR spectra were recorded in the 4000 – 400 cm⁻¹ range on a Perkin Elmer FTIR 1600 Hewlett Packard instrument, using anhydrous KBr pellets. The electronic spectra were performed in 10⁻³ M DMF solutions, with an Ocean Optics spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Results

Elemental analysis for the complex compounds shows that the M:L ratio appears to be 1:1 (as shown in Table 1), suggesting the formulae: [FeCl(CO)(PPh₃)₂L], [FeCl(CO)(PPh₃)₂L'], [FeCl(CO)(PPh₃)₂L''] for the ones with PPh₃ and [FeCl(CO)(AsPh₃)₂L], [FeCl(CO)(AsPh₃)₂L'], [FeCl(CO)(AsPh₃)₂L''] for the ones with AsPh₃.

The compounds obtained are microcrystalline orange powders, whose melting points (m.p.) are higher than the one of the free ligand. They are all stable at room temperature both in solid state and in solution. Their molar electric conductivities showed that all the complexes are non-electrolytes, with molar conductivity values between 6 and 17 Ω⁻¹ cm² mol⁻¹ in 10⁻⁴ M CH₂Cl₂ solutions at room temperature (as presented in Table 1).

Table 1. Analytical data for the three Fe(II) complexes

Compound	m.p. (°C)	Molar Conductance (Ω ⁻¹ cm ² mol ⁻¹)	Analysis (%): calcd./found		
			C	H	N
[FeCl(CO)(PPh ₃) ₂ L]	182	13	69.3(68.8)	4.5(4.5)	1.8(1.7)
[FeCl(CO)(PPh ₃) ₂ L']	176	11	66.9(66.2)	4.7(4.2)	1.5(1.4)
[FeCl(CO)(PPh ₃) ₂ L'']	180	10	69.6(69.8)	4.3(4.1)	1.3(1.2)
[FeCl(CO)(AsPh ₃) ₂ L]	179	15	63.9(63.2)	4.2(4.4)	1.7(1.6)
[FeCl(CO)(AsPh ₃) ₂ L']	170	17	61.8(61.0)	4.4(4.1)	1.6(1.3)
[FeCl(CO)(AsPh ₃) ₂ L'']	176	14	64.3(64.2)	4.0(4.6)	1.5(1.2)

All of the complex compounds are diamagnetic, indicating the (+2) oxidation state of iron.

The results of the spectroscopic study will be given in the next section, as they will be interpreted in order to draw a conclusion regarding the coordination number and consequently the geometry of the complex compounds [3, 4].

3.2. Discussion

All complexes have been by spectroscopically characterized.

The electronic spectra of all the complexes in CH_2Cl_2 display three bands in the 250-530 nm region. One of them - very weak comparing to the others - is assigned to the Laporte forbidden, but vibronically allowed transition $t_{2g}^6 \rightarrow t_{2g}^5 e_g^1$ (the electronic configuration of Fe(II) is d^6 and the octahedral ligand field is strong due to the "back-donation" in which the carbonyl group is involved, making the resultant spin value to be equal to zero – this being the reason why we can be sure of the (+2) state of iron). Taking into account the high extinction coefficients for the other two of them, these bands (around 245 nm and 325 nm) have been assigned to charge transfer transitions arising from promoting an electron from a d level of the metal ion to an unfilled molecular orbital of the Schiff basis (similar assignments have been made for other octahedral Fe(II) complexes).

In the IR spectra of the free Schiff bases, a band of medium intensity appears in the range $3300\text{-}3400\text{ cm}^{-1}$, due to $\nu(\text{O-H})$. This band disappears on complexation with the metal ion, which indicates the deprotonation of each ligand prior to coordination through the oxygen atom. A strong band in the range $1618\text{-}1626\text{ cm}^{-1}$ due to $\nu(\text{C=N})$ undergoes a shift towards lower frequency by $21\text{-}33\text{ cm}^{-1}$ after complexation, indicating the coordination of the nitrogen atom from the azomethine group to the iron ion. A high intensity band occurring at $1282\text{-}1305\text{ cm}^{-1}$ in the free ligands may be assigned to $\nu(\text{C-O})$. In the complexes, the phenolic stretching vibrations are shifted towards higher frequency by $31\text{-}42\text{ cm}^{-1}$, indicating another bonding of the Schiff basis to the metal through the phenolic oxygen atom and consequently proving the monoanionic bidentate nature of

the ligands.

The other characteristic bands, which are basically due to the triphenylphosphine/triphenylarsine (at 1410, 1100 and 700 cm^{-1}) are also present in the spectra of the complexes.

The results presented above about ligand-metal bonding in the new Fe(II) complexes is further supported by the $^1\text{H-NMR}$ spectra. All the complexes show signals in the 7.1 - 7.8 ppm range, due to the phenyl protons of the Schiff basis and also to the triphenylphosphine/ triphenylarsine molecules. The azomethine proton signals in the complexes lie in the 8.2 - 8.8 ppm range. A peak due to the azomethine showed a high field shift compared to the free Schiff base after complexation with the metal ion, indicating coordination through the azomethine's nitrogen atom.

The complete absence of signals due to phenolic protons in the complexes suggests a deprotonation followed by coordination of the phenolic oxygen to the metal center. In addition to the above signals, resonances corresponding to CH_3 protons are also observed in the expected region.

The molecular structure of the three ligands (LH, L'H and L''H) is presented in Figure 1, which also shows that their structures allow them to coordinate to the central metal ion only in their *E* (*entgegen*) form.

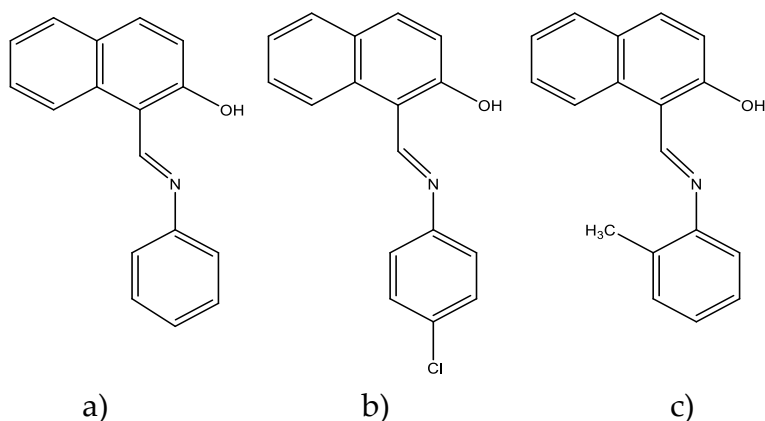


Figure 1. The structure of the three Schiff base ligands:
a) LH=1-((phenylimino)methyl)naphthalen-2-ol;
b) L'H=1-((*p*-chlorophenylimino)methyl)naphthalen-2-ol;
c) L''H=1-((*o*-tolylimino)methyl)naphthalen-2-ol

The suggested molecular structure of the three complexes is presented in Figure 2, where E stands for the corresponding element, *i.e.*, either for P or for As.

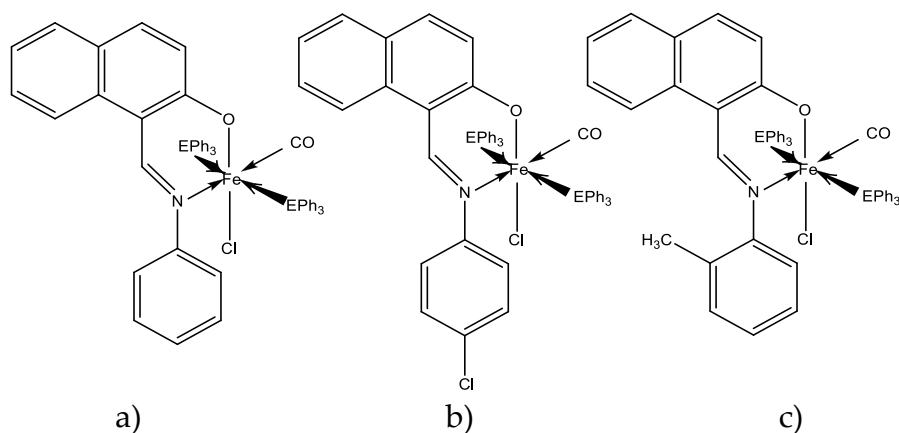


Figure 2. The structure of the three Fe(II) complexes: a) $[\text{FeLCl}(\text{CO})(\text{EPh}_3)_2]$; b) $[\text{FeL}'\text{Cl}(\text{CO})(\text{EPh}_3)_2]$; c) $[\text{FeL}''\text{Cl}(\text{CO})(\text{EPh}_3)_2]$

4. CONCLUSION

In the characteristic IR spectra of the free Schiff bases, a band of medium intensity appears between 3300 and 3400 cm^{-1} , due to the hydroxyl group vibration.

This band disappears after complexation, which indicates a deprotonation of the ligands prior to coordination through the oxygen atom.

Moreover, a high intensity band at 1300 cm^{-1} in the free ligands may be assigned to the phenolic C–O stretching, while in the complexes, C–O stretching vibrations is shifted to higher frequency, confirming the ligand-metal bond through the phenolic oxygen atom.

As expected, a strong band around 1620 cm^{-1} , due to the azomethine group in the free ligands, undergoes a shift to lower frequency by $21\text{--}33\text{ cm}^{-1}$ after complexation, suggesting that the azomethine nitrogen is also coordinated to iron.

These facts prove the uninegative bidentate nature of the ligands.

The other characteristic bands due to triphenylphosphine or triphenylarsine (1410 , 1100 and 700 cm^{-1}) are obviously present in the spectra of the complexes.

The data obtained for the three Fe(II) complexes agree with the proposed molecular formulae where L, L', L'' denote the anions of the Schiff bases, as in all the reactions the Schiff bases behave as anionic bidentate ligands.

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