Solid State Electronic Structure and Properties of Neutral Iron (Fe^{3+}) Complexed Phenalenyl Radicals

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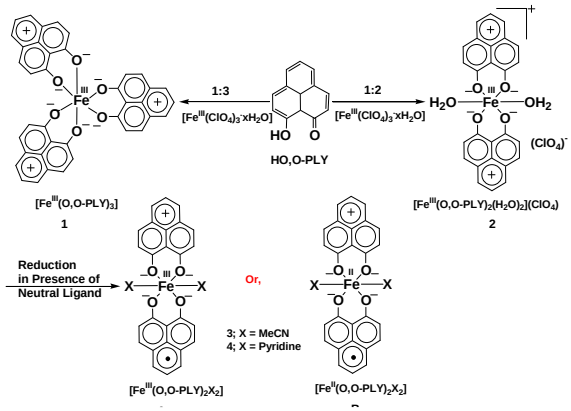
Introduction

Phenalenyl (PLY) is unique in its ability to form stable cations, radicals and anions.[1 - 3] As a result of the delocalization of the unpaired electron throughout the aromatic pi-systems, PLY is potentially capable of undergoing one- and two-electron reduction upon coordination to transition metal centers. Several derivatives of PLY has been designed and their coordination to relatively redox-inert (Al^{III}, Ln^{III}) metals and redox-active (Co^{III}, Fe^{III}, Cr^{III}) transition metals are being explored. In the present report we discuss the application of Mössbauer spectroscopic studies on PLY - iron (III) (Fe^{3+}) complexes.

Experimental

The 1:3 complex (**1**), precursor (**2**) and the radicals (**3, 4**) were synthesized by the following general method. Field-, and temperature-dependent ^{57}Fe Mössbauer spectra were recorded using the constant acceleration Mössbauer spectrometer outfitted with an 8 T superconducting magnet of the EMR facility at NHFML.



Scheme 1.

Results and Discussion

The radical molecules were synthesized by the chemical reduction of the precursor complex **2**, and the reduction was expected to occur at the redox non-innocent phenalenyl unit giving rise to neutral radical molecule **A** (Scheme 1), although we recognized the possibility of reduction at the metal center (Fe^{III} - Fe^{II}) giving rise to neutral molecule **B**. On the other hand binding of a Fe^{III} ion to open shell (redox noninnocent), π-radical ligands such as phenalenyl inevitably induces a strong intramolecular magnetic spin coupling between the non-bonding valence orbitals of the PLY radicals and the metal t_{2g} orbitals of the Fe^{III} ion which may give rise to different electronic ground states depending on the coordinated radicals and the local spin state of the Fe^{III} ion in a given compound. Variable temperature magnetic susceptibility measurements, together with Mössbauer spectroscopic studies are the obvious choice to provide independent spectroscopic information on the local spin and oxidation states of the iron for the above-mentioned compounds (**1**, **3** and **4**). Mössbauer studies indicate that the central metal ion exists as Fe^{III} for the complexes **1** and **3,** whereas the oxidation state of iron in **4** has been reduced to Fe^{II} the in presence of the strong donor ligand. Thus depending on the electron donating ability of the axial ligands, the neutral molecule may either exist in the form of a radical where the central metal is in +3 oxidation state or exist in a non-radical form with iron as Fe^{II}.

Conclusions

We have now synthesized and characterized three iron based phenalenyl compounds: $[Fe^{III}(O, O\text{-}PLY)_3]$ (**1**) $[Fe^{III}(O, O\text{-}PLY)_2(MeCN)_2]$ (**3**), and $[Fe^{II}(O, O\text{-}PLY)_2(Pyridine)_2]$ (**4**), among which the compound **3** is radical (**A**) with an unpaired electron on the PLY ligand. The oxidation states of the central metals were established by Mössbauer studies, and it was shown that compounds **1** and **3** contained Fe (III), whereas **4** contains Fe (II).

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References

[1] Reid, D.H., Chem. Ind., 1504-1505 (1956).
[2] Reid, D.H., Quart. Rev., **19**, 274-302 (1965).
[3] Haddon, R.C., Nature, **256**, 394-396 (1975).