The Electronic Structure of Complexes with Coordinated Organic Radicals

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For any coordination compound, educated chemists can derive a *formal* oxidation number for the central metal ion by applying a given set of rules. It has been taught that you cannot *measure* this formal number since it has no real, physical basis. That's fine. On the other hand, when chemists talk about an iron(III) complex they often imply a well-defined d^n electron configuration (in this case $n = 5$), which is a measurable quantity. In other words, we no longer mean formal oxidation numbers but physical (or spectroscopic) oxidation states (C. K. Jørgensen). In common practice, these two (formal and spectroscopic oxidation numbers) are often used as synonyms – they are not!! The concept of innocent *vs.* non-innocent ligands (C. K. Jørgensen) is accepted by the community but requires the use of physical oxidation numbers.

I will demonstrate how difficult life can be when organic radicals are coordinated to transition metal ions. A classic example is diamagnetic $[Ni(C_6H_4S_2)_2]$ – how should we describe its electronic structure?