

electrons if the energy gap between the a_{1g} and b_{1g} orbitals of the square planar arrangement is large enough to favor the pairing energy. Zn-TPP also led to a negative χ_g value, however because zinc (II) is d10 it matters very little what the energy differences between orbitals are because complete pairing is forced by the presence of 10 d electrons. Cu-TPP, on the other hand, led to a positive χ_g value resulting in a μ_{eff} of 1.506. This μ_{eff} points to the presence of one unpaired electron in this complex, which makes sense because Cu(II) is d9, so when attempting to fill the ten d electron slots there is invariably going to be a lone electron in the highest orbital, regardless of spin.

The visible spectra for TPP and Ni-TPP reveal important information about the binding of ligand to metal as well as offering insight into the symmetry changes of the molecule. The significantly higher molar absorptivity value of the ligand-TPP than the Ni-TPP ($8385.8 \text{ M}^{-1}\text{cm}^{-1}$ for Ni-TPP versus $14186.2 \text{ M}^{-1}\text{cm}^{-1}$) is likely due to changes in bonding chemistry induced by the presence of the metal. The nickel core is capable of powerful backbonding between its d_{π} orbital and the π system of TPP. This backbonding induces a reduction in the ΔE of the $\pi \rightarrow \pi^*$ transition. With a reduction of ΔE comes a reduction in molar absorptivity, explaining the sharp decrease in ϵ from TPP to Ni-TPP.¹ When metal is added to the TPP ring structure, the symmetry of the molecule is increased. The increase in symmetry brought about by the incorporation of a metal in the ring is accompanied by a decrease in the number of peaks and an increase in the simplicity of the peaks.¹

The above principles are demonstrated by the experimental visible region absorption spectra from TPP and Ni-TPP. The spectrum for TPP has four peaks and its high peak is significantly more absorptive than the singular peak of Ni-TPP. These factors combine to suggest that the desired core structure was achieved. The literature values³ for the visible absorption peaks for TPP are 514, 548, 589, and 646nm while the experimental values for TPP were 514, 549, 590, and 646nm. These values are nearly identical, strongly indicating that the correct TPP product was formed.

The NMR spectra can be used to validate the structure of the experimental product and to better understand the downfield shifting induced by the attachment of the nickel atom. The experimental NMR peaks for Ni-TPP are 8.76, 7.99, 7.63, which is very similar to the literature values of 8.73, 7.99, 7.67, and 7.68.³ The integration values for the above NMR were not very accurate to the expected values and the lack of the fourth peak in the 7.6-

Good!

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