The Aldimine Effect in Bis(imino)pyridine Complexes

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Introduction

Bis(imino)pyridine ligands are among the most commonly used ancillary ligands in transition metal catalysis.[1] The success of these ligands can be attributed to their redox non-innocence (ability to accept 1-3 electrons), that facilitates redox transformations at first-row transition metal centers.[2] Several groups have reported that reduction of bis(**ketimino**)pyridine-ligated nickel(II) dihalides invariably forms square-planar nickel(II) products and a ligand-based radical anion. In contrast, we have recently discovered that bis(**aldimino**)pyridines exhibit a significantly different behavior than bis(ketimino)pyridines. Specifically, Fig. 1 demonstrates that the reduced Ni(L)X species are non-planar, which may indicate a significant spin density on the metal.

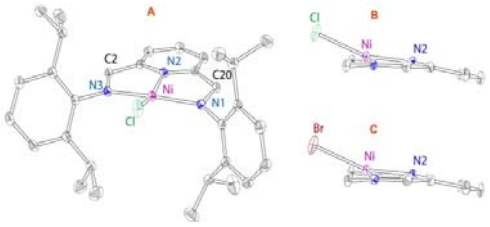

Fig. 1. A: Crystal structures of Ni(L1)Br, top view. B and C: side view of the cores of Ni(L1)Br and Ni(L1)Cl demonstrating the non-planar distortion.

Experimental

A series of high-field EPR measurements were conducted on a ground solid sample of **1** using the homodyne, quasi-optical EPR instrument outfitted with a 15/17T superconducting magnet of the EMR facility

Results and Discussion

A series of variable temperature high-field EPR spectra recorded for **1** at 406.4 GHz are shown in Fig. 2. Inspection of these spectra reveals the presence for this sample of two nearly identical S = 1/2 species which are characterized by rhombic *g* tensors. The presence of two distinct species can be rationalized by the occurrence in the sample of a mixture of **1** and **1a** (a different crystalline form of compound **1** that is also non-planar). The observed *g*-values are considerably larger than $g_e \approx 2.00$ expected for a radical based spin. There are two distinct electronic configurations that could account for our experimental data. Thus, we could either observe a genuine Ni(I) ion with a d^9 configuration or a high-spin Ni(II) ion for which the S = 1 spin of the nickel ion is antiferromagnetically coupled to a S = 1/2 radical based spin. While on the basis of the EPR spectra alone we cannot distinguish between these two possibilities not only are the observed g values well within the range detected for other genuine Ni(I) complexes but also our parallel theoretical investigation strongly supports the presence of a single unpaired electron that is essentially localized on the metal ion.

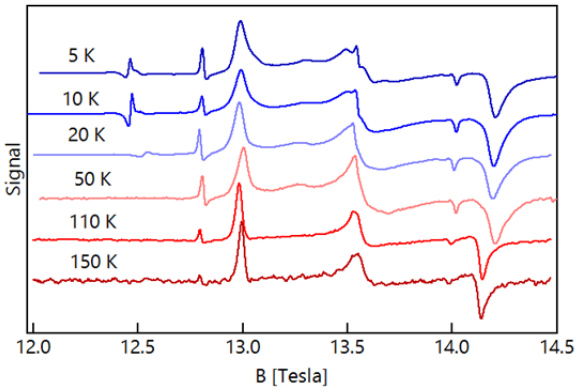

Fig. 2. Variable-temperature high-field EPR spectra recorded for **1** at 406.4 GHz.

Conclusions

Non-planar bis(**aldimino**)pyridine complexes demonstrate a significant spin density at the metal center.

Acknowledgements

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References

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