High-Frequency and -Field EPR of a Titanium(II) Scorpionate Complex

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Introduction

Titanium(II) ($3d^2$) is a relatively rare oxidation state of this metal. It represents the *first* element in the Periodic Table for which a metal-centered multi-electron (i.e., greater than spin doublet) ground state can readily exist in a stable, molecular complex (i.e., as opposed to gas-phase or matrix isolated species). We are therefore interested in investigating by HFEPR representative examples of well-characterized Ti(II) complexes. Among these is the neutral, bis scorpionate complex, [$TiTp_2$], where Tp^- is the original, unadorned scorpionate ligand, tris(pyrazol-1-yl)hydridoborate (Fig. 1).[1] We have also been interested in scorpionate complexes in general,[2] and as such, [$TiTp_2$] represents the earliest d block ion bis scorpionate complex.

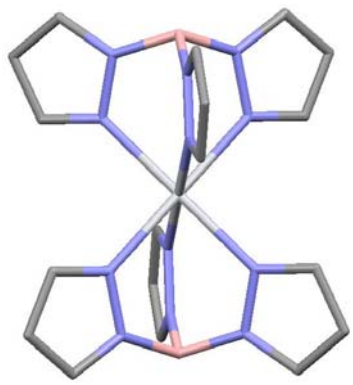

Fig. 1. Molecular structure of [$TiTp_2$]. Pink: B; light blue, Ti; dark grey, C; blue, N. Structure taken from Kayal *et al.*;[1] CSD code: ACOJAD.

Experimental

The DC Facility and its 25 T resistive ("Keck") magnet was used in the experiments. Rigorously air-free procedures were used at all stages for this air-sensitive complex.

Results and Discussion

Powder [$TiTp_2$] generated a strong HFEPR response that could be followed up to 700 GHz. Both the spectra and their frequency dependence could be adequately simulated using a rhombic spin Hamiltonian for a triplet (S = 1) state, with: $|D|$ = 14.5 cm^{-1}, $|E|$ = 0.47 cm^{-1}, and $g_x = g_z$ = 1.9 (g_y is undetermined, possibly due to a field induced torquing effect). The non-trivial rhombic zfs ($|E/D|$ = 0.032) is surprising given that the complex has almost perfect trigonal symmetry (there is a crystallographic inversion center, but no crystallographically imposed trigonal symmetry). The D value is relatively large in magnitude compared to that for the heteroleptic, tetragonal Ti(II) complex, [$TiCl_2(tmeda)_2$] (tmeda = tetramethylethylenediamine), which exhibited D = –5.24 cm^{-1}.[3] However, the D value is indicative that, in contrast to [$TiCl_2(py)_4$] (py = pyridine), the ground state is not orbitally (near)degenerate, i.e., $^3A_2$ not ^3E.

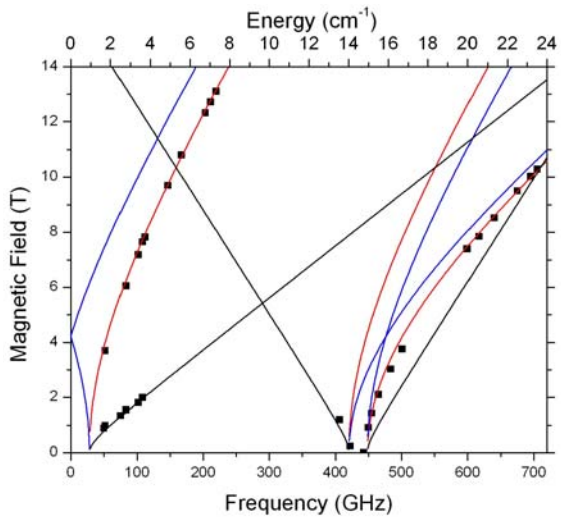

Fig. 2. 2D field/frequency map of resonances in powder sample of [$TiTp_2$] (squares) and its simulation using spin Hamiltonian parameters as in text. Black lines, external magnetic field along molecular z axis; red lines, field along x axis; blue lines, field along y axis.

Conclusions

This study provides electronic structure data on the first S > 1/2 bis scorpionate complex, [$TiTp_2$]. The relatively small size of this complex means that *ab initio* computational methods can be applied to it without truncations, so as to obtain a complete understanding of this fundamental inorganic system.

Acknowledgements

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References

[1] Kayal, A., *et al.*, Chem. Commun., 2482-2483 (2001).
[2] Forshaw, A.P., *et al.*, Inorg. Chem., **52**, 144–159 (2013).
[3] Fortier, S., *et al.*, NHMFL Research Report, 13 (2012).