Isolation of a Triplet Benzene Dianion

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Baird's rule predicts that cyclic molecules with 4*n* π-electrons (*n* = positive integer) should be aromatic in the triplet state; aromaticity implies complete delocalization of the two unpaired electron spins associated with the $S = ½ + ½ = 1$ (triplet) state and an undistorted planar ring system. Unfortunately, efforts to realize such ring systems have been stymied by their tendency to distort into structures favoring a fully spin-paired singlet ($S = 0$) ground state, with a large energy gap to the excited triplet state.

This work demonstrates that the elusive benzene diradical dianion can be stabilized through creation of an unusual metallo-ligand that enforces a tightly constrained inverse sandwich structure, with a metal ion (orange in the Figure) on each face of the central ring system. The benzene dianion possesses two additional electrons in the π-system, i.e., a total of 6 + 2 = 8 π-electrons. High-field EPR measurements were then employed in which the metal ions are non-magnetic yttrium(III), revealing paramagnetic signals consistent with a triplet ($S = 1$) benzene diradical at temperatures down to 5 K. Meanwhile, X-ray diffraction finds aromaticity, consistent with Baird's rule.

This fundamental research demonstrates how molecular symmetry, rigidity and even magnetic exchange coupling can be leveraged to preferentially stabilize and study a desired electronic/magnetic state in an organic molecule.

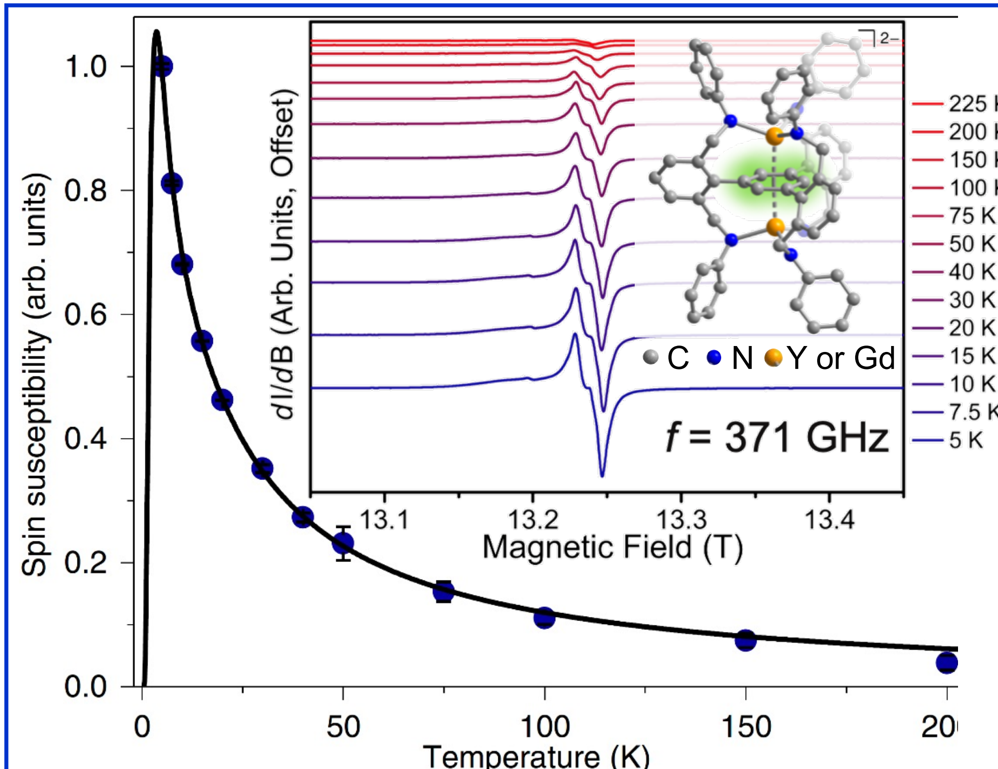

Figure: (main panel) Spin susceptibility deduced from the high-field EPR spectra in the inset, for the compound: $[K(18\text{-crown-}6)(THF)_2]_2[M_2(BzN_6\text{-}Mes)]$ (M = Y, Gd; BzN_6-Mes = 1,3,5-tris[2′,6′-(*N*-mesityl)dimethanamino-4′-*tert*-butylphenyl]benzene), also shown in the inset. The EPR spectra were recorded in derivative mode, *d*I/*d*B, where I is the microwave intensity transmitted through the sample and B the applied magnetic field. The spin susceptibility is obtained via double-integration of the *d*I/*d*B signal.

Facilities and instrumentation used: EMR program, 15/17 Tesla Transmission Spectrometer, 371GHz Microwave Source.

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