Complexes of 1,4,5,8,9,12-hexaazatriphenylene and its hexacarbonitrile derivative

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The tris-chelating ligand 1,4,5,8,9,12-hexaazatriphenylene (HAT) is an interesting candidate for coordination chemistry, but due to the laborious synthesis required to make it and its low solubility in most common solvents, it has not been explored as extensively as other nitrogen-containing heterocycles.\textsuperscript{1,2}

In spite of the inherent problems, chemists began to explore HAT chemistry in the late 1980’s and, since this time, complexes of HAT and its derivatives have been studied in the context of photochemical, supramolecular, magnetic, and biological chemistry.\textsuperscript{1,3} Our particular interest in the HAT molecule and its derivative hexaazatriphenylene-hexacarbonitrile, HAT-(CN)\textsubscript{6}, is to assemble triangular arrangements of paramagnetic metal ions.\textsuperscript{4}
The trigonal geometry of the HAT molecule allows for the formation of trinuclear transition metal complexes which serve as the simplest models of spin-frustrated systems.
DFT Calculations on the Reduced Forms of HAT-(CN)6 and EPR Studies

Neutral HAT-(CN)₆: The Neutral Form of HAT-(CN)₆ optimized to D₃h symmetry, even when the calculation was started with C₁ symmetry.

Monoanion Radical: The lowest energy structure of the mono-anion radical [HAT-(CN)₆]¹⁻ was calculated to have C₂ᵥ symmetry with a ²B₁ electronic state. This distortion from D₃h symmetry is due to a Jahn-Teller distortion from the unstable degenerate ²E'' electronic state to ²B₁.
**DFT Calculations on the Reduced Forms of HAT-(CN)6 and EPR Studies**

**Triplet Dianion Radical (C2v):** This first of 2 lowest energy structures calculated for [HAT-(CN)6]2- has a $^3B_2$ electronic state. This deviation to C2v is due to a second order Jahn-Teller distortion in which the $\alpha$ HOMO e" and the $\alpha$ LUMO a₂" mix.

**Triplet Dianion Racical (D3h):** This second of the 2 lowest energy structures calculated for [HAT-(CN)6]2- has a $^3A_1'$ electronic state.
Singlet Dianion Radical (D<sub>3h</sub>): This <sup>1</sup>A<sub>1</sub> state is higher than the triplet states for [HAT-(CN)6]<sup>2-</sup> but the lowest for the singlet states in general.
The current level of calculations supports the conclusion that the dianion of HAT-(CN)$_6$ is a triplet D$_{3h}$ ($^3A_1$) rather than a triplet C$_{2v}$ ($^3B_2$) or a singlet D$_{3h}$ ($^1A_1$). The monoanion of HAT-(CN)$_6$ shows two different types of hyperfine in its EPR spectrum corresponding to the ring and cyano N atoms; the coupling is weak but could be resolved as indicated by a comparison of the experimental to the simulated spectrum (left figure). The EPR spectrum of the dianion exhibits a forbidden transition in the half-field region at 1685 G (right figure). This corresponds to a $\Delta m_s = 2$ transition that can only originate from a triplet electronic state. The signal in the high field region is due to a collapse of the two allowed $\Delta m_s = \pm 1$ which is expected for very small ZFS.
HAT-(CN)6 + 2 equivalents of Potassium

Half-field Transition

Center Field = 1685 G

High-Field Region
Reactions of HAT-(CN)$_6$ with halide salts were performed and the results of the crystallization of the iodide product are shown in the figures to the right. As the colors in the depicted reaction flasks attest, significant charge-transfer is occurring with [Br$^-$] and [I$^-$]. The reaction with [Cl$^-$] produces a much less dramatic color change. Similar reactions of these anions with HAT do not occur which we attribute to the fact that HAT-(CN)$_6$ is highly electron deficient and is much more likely to participate in donor-acceptor interactions with species such as halides.
Charge Transfer Complexes of HAT-(CN)6 with Halides

\[(n\text{-Bu}_4\text{N})_3\text{[HAT-(CN)}_6\text{]}_2\text{[I]}_3\cdot\text{(C}_6\text{H}_6\text{)}_3\]

\[(n\text{-Bu}_4\text{N})_3\text{[HAT-(CN)}_6\text{]}_2\text{[Br]}_3\cdot3\text{(C}_6\text{H}_6\text{)}\]

R3m  
R1  
= 0.1489  
a = 26.7(1) Å 
b = 26.7(1) Å 
c = 13.7(3) Å

4 Distinct layers arranged along the c axis in columns
Conclusions

• Reactions of HAT and Fe$^{II}$ ions produce a trimer with the HAT ligand acting as a tris-chelating ligand as determined by X-ray studies; the magnetic properties revealed only weak antiferromagnetic exchange.

• Experimental and theoretical results support the conclusion that the dianion of HAT-(CN)$_6$ is a triplet in the ground state.

• Reactions of HAT-(CN)$_6$ with halides lead to intensely colored solutions and crystals with iodide and bromide, an indication of charge-transfer from the anion to the central π-ring.
References


