Inorganica Chimica Acta 361 (2008) 3539–3547

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Electronic structure of $[Ga_2(tren)_2(CA^{sq,cat})](BPh_4)_2(BF_4)$: An EPR, ENDOR, and density functional study

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A R T I C L E I N F O

Article history:
Received 28 February 2008
Accepted 4 March 2008
Available online 18 March 2008

Dedicated to Dante Gatteschi.

Keywords:
EPR
ENDOR
Semiquinone
Gallium
Spin exchange
DFT

A B S T R A C T

The bimetallic $[M_1M_2(tren)_2(CA^{n-})]^{m+}$ series, where M = Ga^{III} or Cr^{III} and CA is the chloranilate ligand which can take on diamagnetic $(CA^{cat,cat})^{4-}$ or paramagnetic $(CA^{sq,cat})^{3-}$ forms, comprises an electronically diverse series of compounds ranging from the closed-shell $[Ga_2(tren)_2(CA^{cat,cat})]^{2+}$ to the $S = 5/2$ ground state of $[Cr_2(tren)_2(CA^{sq,cat})]^{3+}$. This report deals with the interpretation of the EPR and ENDOR spectra of $[Ga_2(tren)_2(CA^{sq,cat})](BPh_4)_2(BF_4)$ (**2**) and the related derivative $[Ga_2(tren)_2(DHBQ)](BPh_4)_2(BF_4)$ (**2a**) (where DHBQ is the fully deprotonated trianionic form of 2,5-dihydroxy-1,4-benzoquinone) in an effort to further characterize the electronic structure of this radical species. The X-band (~9.5 GHz) EPR spectrum of complex **2** acquired in a butyronitrile/propionitrile glass at 4 K reveals a rhombic *g*-tensor with $g_{xx} = 2.0100$, $g_{yy} = 2.0097$, and $g_{zz} = 2.0060$ with hyperfine interactions due to spin delocalization onto the two Ga nuclei ($a_{xx} = 4.902$ G, $a_{yy} = 4.124$ G, $a_{zz} = 3.167$ G); the origin of the hyperfine coupling was confirmed by analysis of the room temperature spectra of complexes **2** and **2a**. The low-temperature spectrum of complex **2** also indicates the presence of a triplet electronic state characterized by a *g*-value of 2.009 and axial zero-field splitting of $D = 150$ G ($0.012\ cm^{-1}$) as determined from measurements carried out at both X- and W-band (~95 GHz) frequencies. This triplet state is believed to arise due to a weak intermolecular Heisenberg exchange interaction between two aggregating complexes. ENDOR measurements on complex **2a** at 20 K allowed for a determination of the magnitude of hyperfine coupling to the protons associated with the radical bridge as well as providing a rare example of an ENDOR signal arising from coupling to a gallium nucleus. Finally, these results were combined with literature data on the free semiquinone form of the bridging ligand in order to assess the extent to which density functional theory can predict unpaired spin density distribution in a complex molecule of this type. Although differences between theory and experiment were noted, DFT was able to provide a reasonably accurate picture of the electronic structure of this system as well as provide insight into the spin polarization mechanism(s) responsible for the observed hyperfine interactions.

1. Introduction

Few researchers have had as significant an impact on their field as Professor Dante Gatteschi has in the area of molecular magnetism. From early work on the properties of small molecules to his pioneering efforts developing the concept of single-molecule magnetism, Professor Gatteschi's seminal contributions have literally defined a field that now comprises the scientific endeavors of dozens of research groups throughout the world. It is an honor to be asked to contribute to this Special Issue of *Inorganica Chimica Acta* recognizing the wonderful career of Professor Gatteschi.

One of our research programs pertaining to the field of magnetism is focused on developing an understanding of the effects of Heisenberg spin exchange interactions on the photophysical properties of molecules. Metal–quinone complexes – a class of compounds on which Professor Gatteschi has published a number of important papers – constitute a convenient platform for these efforts insofar as the redox activity of the quinone ligand provides a facile mechanism for turning exchange interactions "on" (i.e., paramagnetic semiquinone) or "off" (diamagnetic catechol). By exploiting this inherent redox-based tunability, we wish to define and differentiate properties endemic to the constituents of the molecule from those that arise due to exchange interactions among them. Toward this end, we recently reported on the synthesis and spectroscopic properties of the $[M_1M_2(tren)_2(CA^{n-})]^{m+}$ series, where M = Ga^{III} or Cr^{III}, tren is tris(2-aminoethyl)amine, and CA^{n-} is the deprotonated form of chloranilic acid which acts as a bridging chelate between the two metal ions [1]. The chloranilate ion can be stabilized in a variety of oxidation states (Chart 1):

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doi:10.1016/j.ica.2008.03.021

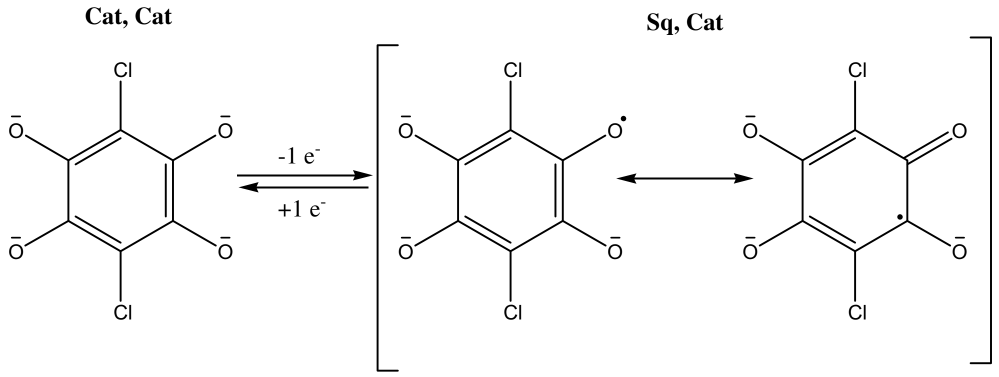

Chart 1.

systematic incorporation of Cr^{III} (d^3, $S = 3/2$) and/or Ga^{III} (d^{10}, $S = 0$) coupled with the 4- and/or 3-forms of chloranilate yielded a series of six complexes (Chart 2) whose magnetic, electrochemical, and optical properties were described in detail. In particular, magnetic susceptibility data revealed a variety of magnetic ground states across this series ranging from the singlet ($S = 0$) ground state of compound **1** to the sextet ($S = 5/2$) ground state of compound **6**. With this information in hand, we sought to develop a more comprehensive picture of the electronic structures of these compounds through the use of electron paramagnetic resonance (EPR) spectroscopy.

A logical starting point for our work is complex **2**, the simplest paramagnetic member of the series consisting of two diamagnetic metal centers bridged by the semiquinone ligand radical $[CA^{sq,cat}]^{3-}$. EPR has previously been implemented to characterize the ground states of metal–semiquinone complexes incorporating diamagnetic metals. For example, Tuck and co-workers have prepared Ga^{III} complexes of the 3,5-di-*tert*-butyl-1,2-benzosemiquinonate anion species and examined them via X-band EPR [2]. Wieghardt's group has synthesized and studied the magnetic properties of a series of metal complexes, including Ga^{III}, with a phenoxy radical ligand [3]. More recently, Baker et al. have carried out synthetic, EPR and electron nuclear double resonance (ENDOR) studies on a series of Ga^{III}, In^{III}, and Al^{III} complexes of the radical anion of diazabutadiene [4–6]. In all of these cases hyperfine coupling to the metal (^{27}Al, $^{69,71}Ga$ and/or ^{115}In) was observed; room temperature X-band spectra of the Ga^{III} complexes were simulated with different isotropic hyperfine couplings from the different Gallium isotopes. Other semiquinone species have been prepared with diamagnetic metal cations such as closed-shell alkali and alkaline earth cations [7,8]. A common theme in many of these studies is a certain degree of spin delocalization onto the metal center, giving rise to weak but measurable hyperfine interactions stemming from the interaction of the electronic spin with the metal nuclei.

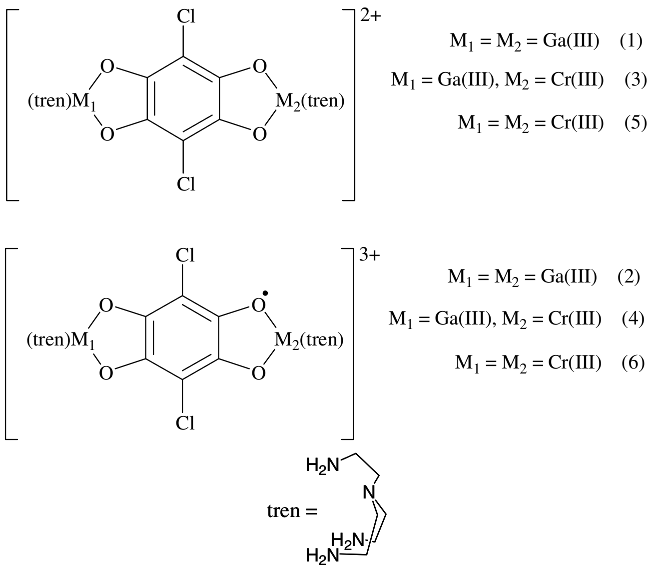

Chart 2.

Herein, we describe the results of a variable-field, variable-temperature EPR study of $[Ga_2(tren)_2(CA^{sq,cat})](BPh_4)_2(BF_4)$ (**2**) and its related derivative $[Ga_2(tren)_2(DHBQ)](BPh_4)_2(BF_4)$ (**2a**) (where DHBQ is the fully deprotonated form of 2,5-dihydroxy-1,4-benzosemiquinone). Accurate simulations of the various spectra have enabled us to characterize in detail the $S = 1/2$ ground state of this system and quantify the hyperfine interactions that exist between the organic radical and the ligated metal ions. ENDOR measurements on complex **2a** have provided information on hyperfine coupling between the π-based organic radical and the symmetry-related protons of the DHBQ bridge, as well as revealing a signal arising from hyperfine interactions involving the Gallium nuclei. Finally, density functional theory has been employed to assess the extent to which calculations of spin density distributions in an organic/inorganic hybrid system such as this correlate with values obtained directly from experiment.

2. Experimental

2.1. General

All reagents and materials were used as received unless otherwise noted. Solvents were purchased from Aldrich Chemical Co. and distilled and degassed by the freeze-pump-thaw method. The ligand tris(2-aminoethyl)amine (tren) was purchased from Aldrich and vacuum-distilled prior to use. All synthetic procedures involving hydrochloranilic acid and 1,2,4,5-tetrahydroxybenzene were performed under an inert atmosphere. $[Fe(Cp^*)_2](BF_4)$ was prepared according to literature methods [9]. Hydrochloranilic acid and 1,2,4,5-tetrahydroxybenzene was synthesized by a modification of a previously reported method [10,11]. $Ga(tren)(NO_3)_3$ and $[Ga_2(tren)_2(CA^{sq,cat})](BPh_4)_2(BF_4)$ were prepared as previously described [1].

2.2. *$[Ga_2(tren)_2(DHBQ)](BPh_4)_2(BF_4)$ (**2a**)*

Under N_2, 1,2,4,5-tetrahydroxybenzene (1.00 mmol, 0.142 g) and triethylamine (4.00 mmol, 0.404 g) were dissolved in 100 mL of degassed methanol. This solution was added dropwise into a solution of $Ga(tren)(NO_3)_3$ (1.80 mmol, 0.724 g) in 80 mL of meth-