J. Am. Chem. Soc. 1987, 109, 5272–5273

A Copper(II) Dope as a Detector for the High-Spin ↔ Low-Spin Transition in the Two-Dimensional Compound [*trans*-Bis(thiocyanato)bis(4,4′-bi-1,2,4-triazole)iron] Hydrate

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Received March 31, 1987

High-spin ↔ low-spin transitions of divalent iron(II) or other first-row transition-metal ions with d^4 to d^7 electron configurations have been studied for many years. Several techniques are available to investigate this phenomenon. Mössbauer spectroscopy, magnetic measurements, heat capacity, X-ray diffraction techniques, and UV–vis and infrared spectroscopy have been used and were discussed in several review articles.[1]

These techniques all focus either on the metal species, which undergoes the transition, i.e., its electronic and magnetic properties, or on changes in the lattice accompanying the spin crossover, as revealed by heat capacity data and X-ray diffraction patterns, or on species which are by definition present in the compound, i.e., counterions and ligands. In principle, it should be possible, however, to introduce a guest species in the compound, the behavior of which is drastically changed when the host compound undergoes the spin transition, and to focus on that species with variable temperature physical measurements to detect the spin transition. In this way the crossover phenomenon can be observed indirectly.

Two-dimensional $[Fe(NCS)_2(btr)_2]{\cdot}H_2O$ (btr = 4,4′-bi-1,2,4-triazole) was reported to exhibit a high-spin ↔ low-spin transition around 150 K, and the structure of the X-ray isomorphous cobalt compound has been solved.[2] $[Fe(NCS)_2(btr)_2]{\cdot}H_2O$ is the first spin-transition iron compound with trans-oriented thiocyanate groups and ligand-bridged iron atoms. The local symmetry of the metal ion is almost D_{4h}, which is an environment suited for Cu(II) ions. Because the metal ions are connected by bitriazole bridges, it is to be expected that the spin transition of the iron ions will effect the magnetic properties of doped metal ions, such as Cu(II) and, thus, the EPR spectrum of the compound. A copper dope of $[Fe(NCS)_2(btr)_2]{\cdot}H_2O$ has been synthesized.[3]

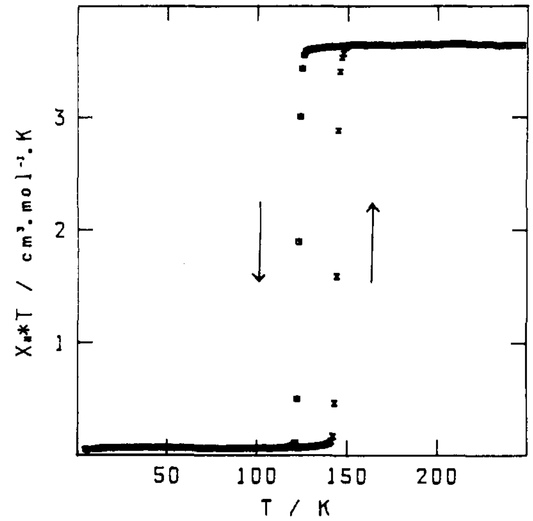

Figure 1. $\chi_M T$ vs. temperature curves of copper-doped $[Fe(NCS)_2(btr)_2]{\cdot}H_2O$.

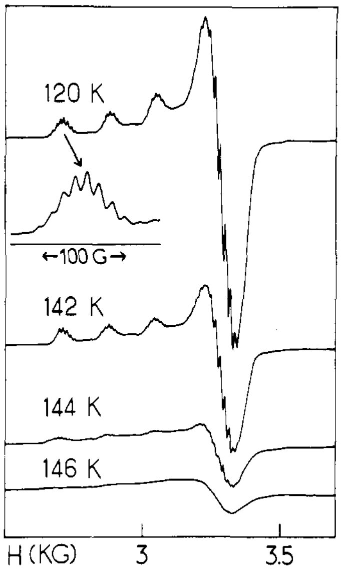

Figure 2. EPR spectra of copper-doped $[Fe(NCS)_2(btr)_2]{\cdot}H_2O$ as a function of increasing temperature.

The $\chi_M T$ vs. T plots[4] for the copper-doped species are shown in Figure 1. The curves exhibit a very abrupt and complete spin transition with transition temperatures $T_c{\downarrow} = 123.5$ K when cooling the sample and $T_c{\uparrow} = 144.5$ K when heating it. The hysteresis range is therefore 21 K, and the same magnetic behavior was obtained with the undoped species.

Because of the completeness of the transition the host lattice becomes essentially diamagnetic below T_c, whereas it is paramagnetic above T_c. Therefore, large differences could be expected between the EPR spectra of this compound above and below T_c. EPR spectra as a function of increasing temperature[5] are presented in Figure 2. In the paramagnetic phase the EPR spectrum is very poorly resolved due to exchange broadening. It shows a broad signal at $g = 2.1$ and additional weak signals at $g = 4.7$ and $g = 3.4$. In contrast, at T_c and below, a beautifully resolved spectrum is observed corresponding to a magnetically isolated copper(II) ion in an elongated tetragonal environment ($g_\perp = 2.05$, $g_\parallel = 2.29$) with hyperfine structure ($A = 165$ G) as well as superhyperfine structure ($A_{N\parallel} = 13.7$ G, $A_{N\perp} = 17.1$ G). The superhyperfine structure splits each line into nine components, which shows that the unpaired electron of copper(II) in the $d_{x^2-y^2}$ orbital only couples with the four nitrogen atoms from the triazole rings located in the basal plane. The replacement of iron(II) by

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(3) Cu(II)-doped $[Fe(NCS)_2(btr)_2]{\cdot}H_2O$ was prepared by adding a hot solution of 0.1 mmol of $CuCl_2{\cdot}2H_2O$ in 5 mL of water to a hot solution of 1 mmol of $FeCl_2{\cdot}4H_2O$, 2 mmol of btr, and 2 mmol of NH_4NCS in 20 mL of water. The latter solution had been treated with SO_2 to reduce eventually formed trivalent iron ions. Upon adding the copper chloride solution a precipitate was formed which was removed by filtration. Upon standing at room temperature crystals were formed within a day. Metal analyses were performed by using atomic absorption techniques: Fe:Cu = 1:0.11. The compound has the same X-ray powder and infrared patterns as the undoped compound. Infrared spectra (4000-180 cm^{-1}) were recorded as Nujol mulls on a Perkin-Elmer 580 spectrophotometer. A Guinier–de Wolff camera was used to obtain X-ray diffraction patterns.

(4) Magnetic susceptibilities were recorded by using a Faraday type magnetometer equipped with a He continuous-flow cryostat working in the 2–300 K temperature range. χ_M is the molar magnetic susceptibility corrected for the small amount of copper(II) ($\chi_M^{Cu}T = 0.042$ cm³ mol⁻¹ K) and for the diamagnetism estimated as -130×10^{-6} cm³ mol⁻¹.

(5) The EPR spectra were recorded at X-band frequencies with a Bruker ER 200D spectrometer equipped with an Oxford Instruments continuous-flow cryostat. The temperature control of the EPR spectrometer did only allow accurate measurements in the heating mode.

0002-7863/87/1509-5272$01.50/0

copper(II) distorts the site that adopts the usual 4 + 2 geometry with an apparent lengthening of the Cu-N(CS) apical bonds. Rao et al.[6] detected the HS $\leftrightarrow$ LS transition with EPR spectroscopy on a guest ion, by preparing Mn-doped [Fe(phen)$_2$(NCS)$_2$] and [Fe(pic)$_3$]Cl$_2$·EtOH (pic = 2-(aminomethyl)pyridine. However, only a broadening of the EPR resonance lines at the transition temperature was observed.

The present study surprisingly shows that it is quite possible to detect the HS $\leftrightarrow$ LS transition in an iron compound by focussing on the EPR spectrum of a doped species, which acts as a "spy" to get information about the spin state of the host lattice. A copper(II) may be used in other systems. So, an effect comparable to that described above was observed for a Cu(II) doped [Fe(1-propyltetrazole)$_6$](BF$_4$)$_2$. Other EPR active ions may also be utilized. Preliminary results indicate that the EPR spectrum of a Mn(II) doped [Fe(NCS)$_2$(btr)$_2$](H$_2$O) also shows an abrupt change at T_c. The now described method of detecting spin crossover phenomena is not restricted to magnetically coupled systems. Detailed information on these two systems will be presented in later work.

Acknowledgment. The present investigations were carried out with support from the Netherlands Foundation for Chemical Research (SON) and with financial aid from the Netherlands Organization for Pure Research (ZWO) through project 11-28-17.

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Multiple Deprotonation of a Ferraborane. Evidence for the Formation of a Discrete Transition-Metal Boride

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Received March 16, 1987

Discrete molecular clusters containing interstitial carbon atoms are now well known,[1] and the structural types observed mimic some of the solid state carbides. Although all clusters with interstitial atoms thus far identified contain electron precise, e.g., C, or electron rich, e.g., N, O,[2] atoms, there is no a priori reason why boron should not be found as an interstitial element in transition-metal clusters. Indeed metal borides are well known in the solid state[3] and exhibit a variety of structural types containing periodic units of one or more boron atoms. In the following, we present definitive evidence for the formation of a species containing a bare boron partially surrounded by metal atoms which is isoelectronic with an exposed iron carbide cluster.[4]

The exhaustive deprotonation of a metal-rich metallaborane provides an obvious route to a boride. However, small boranes are not known for ease of deprotonation.[5] The same is true of hydrocarbons, but the presence of a transition metal alters the situation considerably. For example, HFe$_4$(CO)$_{12}$CH yields a carbido cluster dianion on double deprotonation,[6] and we have already reported the facile single deprotonation of HFe$_4$(CO)$_{12}$BH$_2$, I, the isoelectronic analogue of HFe$_4$(CO)$_{12}$CH.[7] The PPN salt of [HFe$_4$(CO)$_{12}$BH]$^-$, II, resists further attempts at deprotonation, but we have now found that multiple deprotonation of I with butyllithium or further deprotonation of the alkali metal

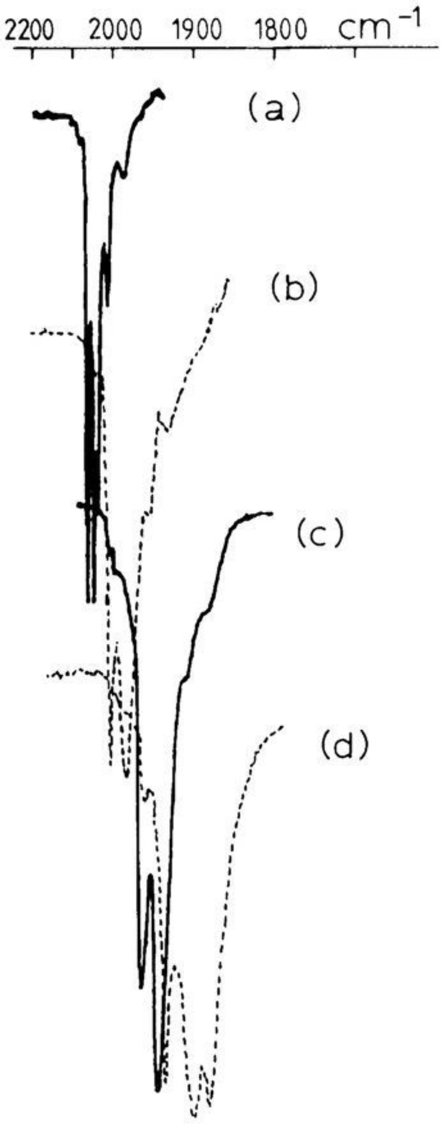
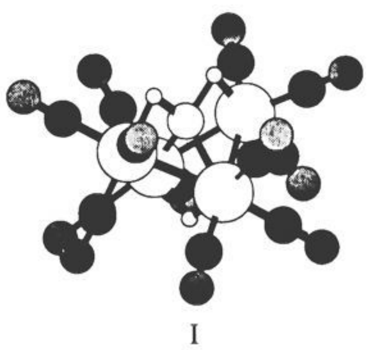
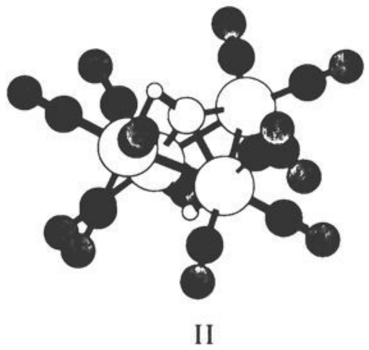


Figure 1. Infrared spectra of (a) I, (b) II, (c) III, and (d) IV (A small amount of III is present.).

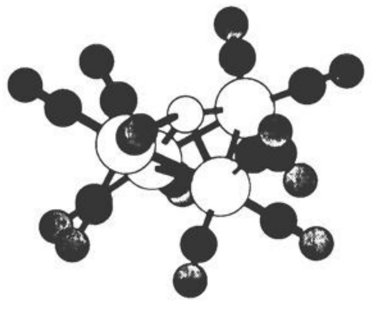


I



II

III



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