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^{57}Fe Mössbauer study of an iron(II) sensor for the detection of toxic gases at room temperature

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Abstract
We present herein the magnetic and Mössbauer investigation of a colorimetric chemical sensor with the chemical formula $[Fe(H_2btm)_2(H_2O)_2]Cl_2$ (**1**) (***H_2btm*** = Di(1H-tetrazol-5-yl)methane). The spectra were recorded before and after sensing a series of toxic gases (MeOH, diethylenetriamine, hexylamine, 1,2-diaminocyclohexane, 3-picolylamine, pyridine and furfurylamine). Worth to note that the sensing process (color changes) proceeds at room temperature, does not require any pretreatment and can be detected as well by the naked eyes. ^{57}Fe Mössbauer spectroscopy not only allows to identify the nature of spin states involved in our Fe(II) sensor but also to evaluate quantitatively the respective spin state population, i.e. high spin and low-spin states.

Keywords Colorimetric chemosensor · Magnetic properties · Spin states · ^{57}Fe Mössbauer spectroscopy

1 Introduction

On one hand, the increasing demand for human life has led to expanding exploitation and consumption of energy, which in turn releases a large amount of harmful and toxic gases. Toxic gases not only pollute the environment where we live, but also have a great impact on our health [1, 2]. For example, they are irritating to the eyes, respiratory tract mucosa and skin to varying degrees. Among them, a wide range of amine organics are considered as pollutants in the industrial and manufacturing fields because they are widely used in the preparation of herbicides, fertilizers, latexes, drugs, surfactants, biological buffer substances and colorants [3]. When the concentration of amine gas reaches a certain level,

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people will feel uncomfortable, which can cause nausea and vomiting, allergy and cancer issues, and even death [1, 2]. In order to establish a healthy and friendly living environment, it is urgent to develop simple and convenient ways to detect toxic and harmful gases in the environment.

The conventional gas-phase detection methods for toxic gases (TGs) in the air are mainly GC and GC-MS. [4] Currently, according to the different materials encountered in existing sensors, sensors can be divided into the following categories: (1) Metal Oxide Semiconductor (MOS) sensors [5–7] such as ZnO, SnO_2, WO_3, etc. When gas molecules are adsorbed, the oxide resistivity drop. Such methodology requires heating and therefore consumes energy. (2) Mass sensor (Quartz Crystal Microbalance, QCM) [8]: after adsorbing gas molecules, the vibration frequency of quartz crystal will change. However, such sensor usually leads to poor selectivity. (3) Optical sensor [9]: when the sensor interacts with the analyte gas molecules, the optical properties are modified. For example, the refractive index (with a refractive index measuring instrument) [10], the fluorescence intensity [11] (fluorescence measuring instrument) or simply the color [12–16]. Among them, colorimetric sensors are considered as the best sensors. Ideally, low-cost sensors working at room temperature, not requiring any preheating, environmentally friendly, easy to operate, and offering an excellent and fast detection performance are considered as a research target of analytical chemists all over the world.

Recently we identified one such of these materials of the following formula $[Fe(H_2btm)_2(H_2O)_2]Cl_2$ (**1**) (***H_2btm*** = Di(1H-tetrazol-5-yl)methane). After adsorption of different TGs, especially, amine organic gas molecules, the sensor can display different colors and which can be distinguished by the naked eye at room temperature without any equipment [17]. In the following report, we will go into detail into the Mössbauer (and magnetic) study of this sensor before and after gas exposure of a series of guest molecules. Whereas magnetic measurements show that they all exhibit characteristic paramagnetic behavior from room temperature down to liquid helium temperature, ^{57}Fe Mössbauer spectroscopy allowed to track an unexpected spin state change at room temperature upon guest molecules adsorption.

2 Experimental

All chemicals and solvents were purchased from commercial sources of analytical grade and used without further purification. In order to increase the specific surface area of the sensor and to reduce the detection time, we therefore mechanically grind the crystals after guest adsorption leading to **1**@MeOH, **1**@diethylenetriamine, **1**@hexylamine, **1**@1,2-diaminocyclohexane, **1**@3-picolylamine, **1**@pyridine and **1**@furfurylamine. Magnetic susceptibilities were measured on a Quantum design MPMS-5 s SQUID magnetometer. Magnetic data were corrected for the sample holder and diamagnetic contributions. The crystal sample was quickly loaded into a gelatin capsule and immediately inserted within the SQUID cavity. ^{57}Fe Mössbauer spectra were recorded in transmission geometry with a constant acceleration mode conventional spectrometer equipped with a 50 mCi ^{57}Co(Rh) source and a Reuter Stokes proportional counter. The powdered samples were sealed in aluminum foil and spectra were recorded at 298 K. The spectra were fitted using Recoil 1.05 Mössbauer Analysis software (K. Lagarec, D. G. Rancourt, Recoil, Mössbauer Spectral Analysis software for Windows 1.0, Department of Physics, University of Ottawa, 1998). The isomer shift values are given with respect to α-Fe at room temperature.

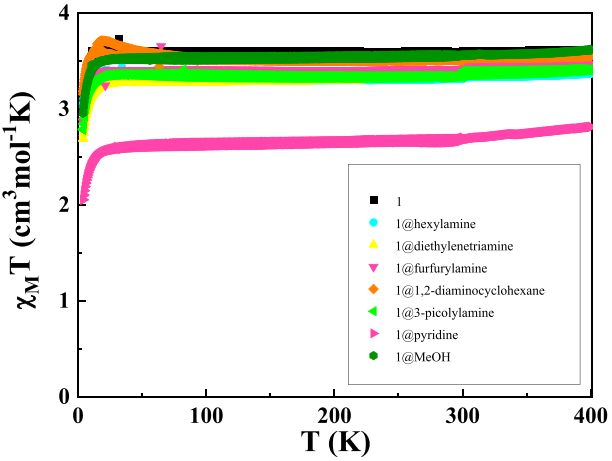

Fig. 1 Temperature-dependent $\chi_M T$ plots for **1** before and after adsorption of different guest molecules

3 Results and discussion

The samples in polycrystalline form were studied by SQUID magnetometry before and after guest adsorption over the range 4–400 K under a constant field of 1 T. Systematically, lower $\chi_M T$ values, χ_M being the molar magnetic susceptibility, were observed for samples after adsorption compared to **1** at 298 K, which shows a full paramagnetic state with $\chi_M T = 3.60$ cm^3 K mol^{-1} (Fig. 1). This value is typical for high-spin (HS) Fe(II) ions, and consistent with the observations from single crystal X-ray diffraction, which revealed a FeN_4O_2 coordination sphere [17]. Remarkably, **1**@pyridine, showed an obvious reduce of its $\chi_M T$ value down to $\chi_M T = 2.67$ cm^3 K mol^{-1} at 300 K, thus indicating still a large fraction (~ 30%) of HS Fe(II) ions ($S = 2$), but most presumably with a fraction of low-spin (LS) Fe(II) ions ($S = 0$). When sensors before and after adsorption of TGs were cooled, $\chi_M T$ values remained overall constant until a sudden drop occurred below 20 K, which was attributed to zero-field splitting of HS Fe (II) ions.

A series of ^{57}Fe Mössbauer spectra of **1** were recorded before and after guest molecules inclusion at room temperature (Fig. 2). A quantitative analysis of spin state and oxidation state was undertaken too (Fig. 3). ^{57}Fe Mössbauer spectrum of **1**, at 298 K, shows one quadrupole doublet with an isomer shift $\delta = 1.15(1)$ mm s^{-1} and a quadrupole splitting $\Delta E_Q = 3.66(1)$ mm s^{-1} of area fraction A = 100%, which are characteristics of HS Fe(II) ions (Fig. 2a). After adsorbing hexylamine$_{(g)}$ molecules, a new quadrupole doublet emerges in the center [$\delta = 0.36$ (4) mm s^{-1}; $\Delta E_Q = 0.26(1)$ mm s^{-1}] of area fraction A = 9%, in the spectrum of **1**@hexylamine (Fig. 2d), which are characteristic of LS Fe(II) ions. A quadrupole doublet was also identified for **1**@pyridine with $\delta = 0.14(1)$ mm s^{-1} and $\Delta E_Q = 0.62$ (2) mm s^{-1}, whereas a singlet was observed for **1**@MeOH, **1**@diethylenetriamine, **1**@3-picolylamine, **1**@1,2-diaminocyclohexane and **1**@furfurylamine, at $\delta \sim 0.38$ mm s^{-1} with area fraction ~14% (Fig. 3d). This signal points out unambiguously to LS Fe(II) ions after adsorption, with parameters characteristic of Fe(II) ions being set in a FeN_6 core [12]. This explains the decrease of isomer shift compared to $\delta = 1.15(1)$ mm s^{-1} for **1**, as a result of the replacement of oxygen atoms by nitrogen atoms, which are less electronegative, and thereby increases the electronic density of s electrons in the vicinity of the iron nucleus and therefore lower the isomer shift [13]. Furthermore, the radius of nitrogen atoms which is smaller than that of oxygen

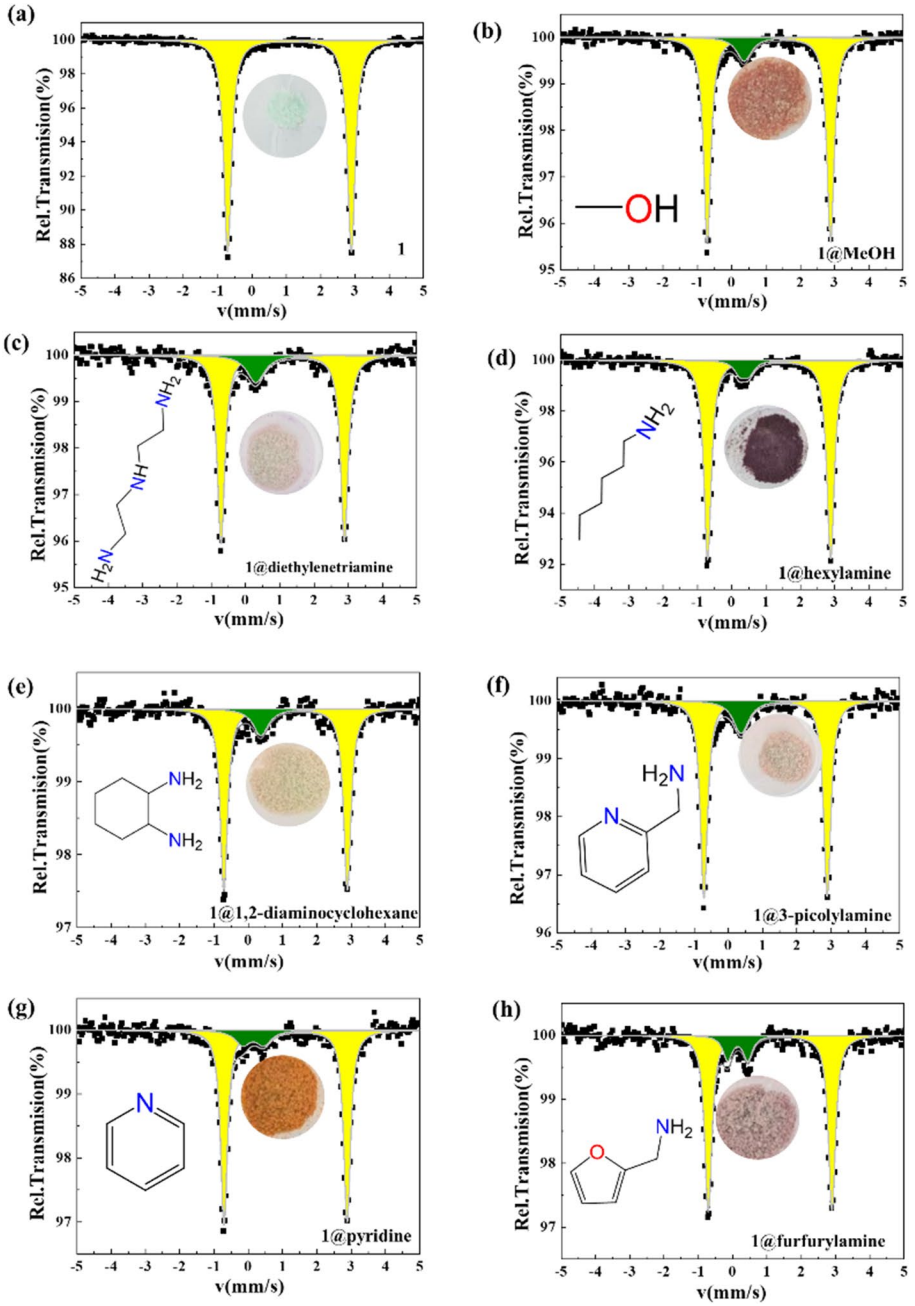

Fig. 2 ^{57}Fe Mössbauer spectra at room temperature for (**a**) **1**; (**b**) **1**@MeOH; (**c**) 1@diethylenetriamine; (**d**) **1**@hexylamine; (**e**) **1**@1,2-diaminocyclohexane; (**f**) **1**@3-picolylamine; (**g**) **1**@pyridine; (**h**) **1**@furfurylamine. The discrepancy observed with **1**@pyridine after SQUID in term of LS population (~30% vs 14% (Mössbauer)) is due to the different guest time exposure which was less for the samples studied by Mössbauer (less than 2 h)

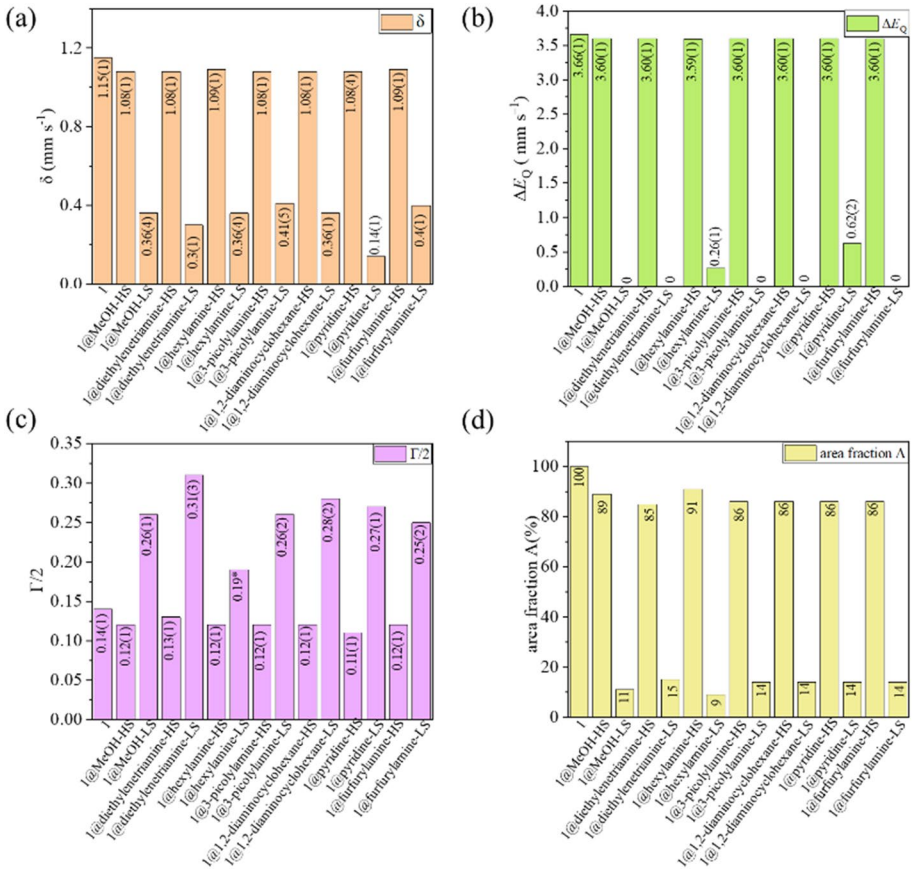

Fig. 3 Overview of ^{57}Fe Mössbauer parameters (δ (mm s^{-1}), ΔE_Q (mm s^{-1}), $\Gamma/2$ and % of species) for **1**, **1**@MeOH, **1**@1,2-diaminopropane, **1**@diethylenetriamine, **1**@hexylamine, **1**@3-picolylamine, **1**@1,2-diaminocyclohexane, **1**@pyridine, **1**@furfurylamine at room temperature. (δ: isomer shift (r.t., vs. α-Fe); ΔE_Q: quadrupole splitting, $\Gamma/2$: half width at half maximum, *fixed parameter)

atoms, and their lower electronegativity eases the formation of a strong coordination bond between N and Fe(II) ions. Thereby constructing a LS FeN_6 core upon guest adsorption. In the case of methanol, this occurs too but through an allosteric mechanism involving the formation of intermediate species and coordination of neighboring ligands providing their N atoms [14].

4 Conclusions

In summary, we report on the study of a mononuclear Fe(II) complex which acts as a sensor after adsorption of toxic gases at room temperature. In addition to a remarkable color change, which can be detected by the naked eyes, a quantification of the spin state population was undertaken thanks to ^{57}Fe Mössbauer spectroscopy. As a result, our sensor was shown to exhibit excellent performance for the detection of toxic gases and hazardous

chemicals at room temperature, due to a part of high-spin Fe(II) ions converting to the low-spin state after adsorption is completed.

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