

Gold-surface binding of molecular switches studied by Mössbauer spectroscopy

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Abstract The nonanuclear coordination compound $[\text{Mo}^{\text{IV}}\{(\text{CN})\text{Fe}^{\text{III}}(3\text{-methylsaldptn})\}_8]\text{Cl}_4$ exhibits multiple spin transitions (3-methylsaldptn = N,N'-bis(3''-methyl-2''-hydroxy-benzyliden)-1,7-diamino-4-azaheptane). This spin crossover cluster is bound via a self-assembled monolayer onto a two dimensional array gold surface. Mössbauer spectroscopy indicates that the thermally and optically induced spin crossover of the compound is maintained. Thereby, the foundation for its potential practical application (e.g. in the field of information storage) was laid.

Keywords Nonanuclear · Spin crossover · Au surface · Self-assembled monolayer · Mössbauer spectroscopy

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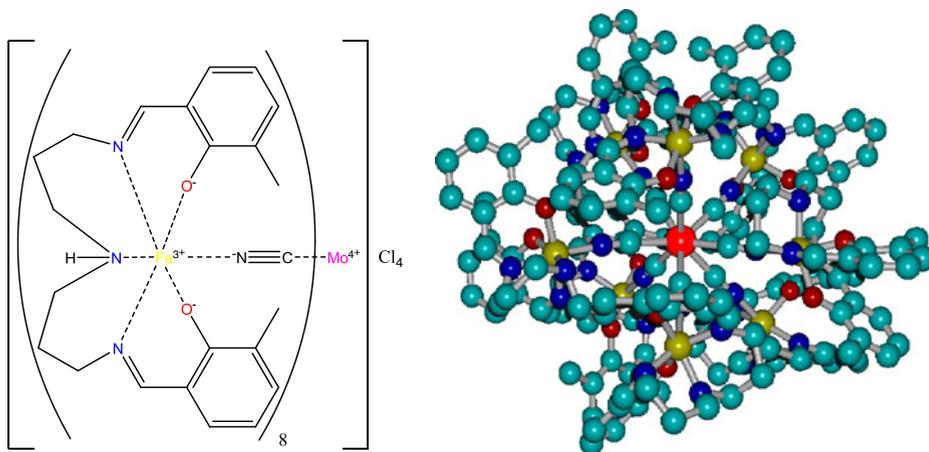


Fig. 1 Structural formula of $[\text{Mo}^{\text{IV}}\{(\text{CN})\text{Fe}^{\text{III}}(3\text{-methyl-saldptn})\}_8]\text{Cl}_4$ **1** (left), Hyperchem 7 (MM+) calculated structure of the cation (right); hydrogen atoms are omitted for clarity

1 Introduction

The spin crossover is one of the most fascinating dynamic phenomena known in coordination chemistry. In this research area, switching between high spin and low spin states of a transition metal complex can be induced physically (e.g. by varying the temperature, applying pressure or through irradiation with light) or chemically (e.g. through solvate effects or pH influences) [1–4]. Recently, there has been interest in multinuclear systems in which an interplay between a spin crossover effect and magnetic exchange interactions occurs [5–8]. Among them is the star-shaped nonanuclear coordination compound $[\text{Mo}^{\text{IV}}\{(\text{CN})\text{Fe}^{\text{III}}(3\text{-methyl-saldptn})\}_8]\text{Cl}_4$ **1** (3-methyl-saldptn = N,N'-bis(3''-methyl-2''-hydroxy-benzylidene)-1,7-diamino-4-azaheptane) (Fig. 1) [9–11].

Within **1** each iron center is potentially able to exhibit a thermally and optically induced spin crossover between the low-spin (LS; ^2T ; $S = 1/2$) and the high-spin (HS; ^6A ; $S = 5/2$) state [8–11]. Hence, **1** may contain between 8 and 40 unpaired electrons and offers a maximum of 8 potential spin transitions.

Many potential technical applications (e.g. in the field of information storage) require an individual addressing of these special molecular magnets, which is imaging, reading and eventually the manipulation of the molecules. In this instance, the concept of the self-assembled monolayers provides a suitable basis in order to obtain a monolayer of the spin crossover compound on various substrates [12].

In this case, a smooth gold surface was chosen due to its relatively inertness, the easy preparation, the well-defined order and since it offers the possibility of addressing the clusters individually by scanning probe microscopy (atomic force microscopy). Furthermore, an adsorption process onto a thin gold surface can be monitored by surface plasmon resonance spectroscopy [13].

The observation of the surface binding by surface plasmon resonance as well as the nanoscopic appearance of the individual nonanuclear complexes displayed by AFM and TEM imaging would exceed the extend of this article and will be published soon.

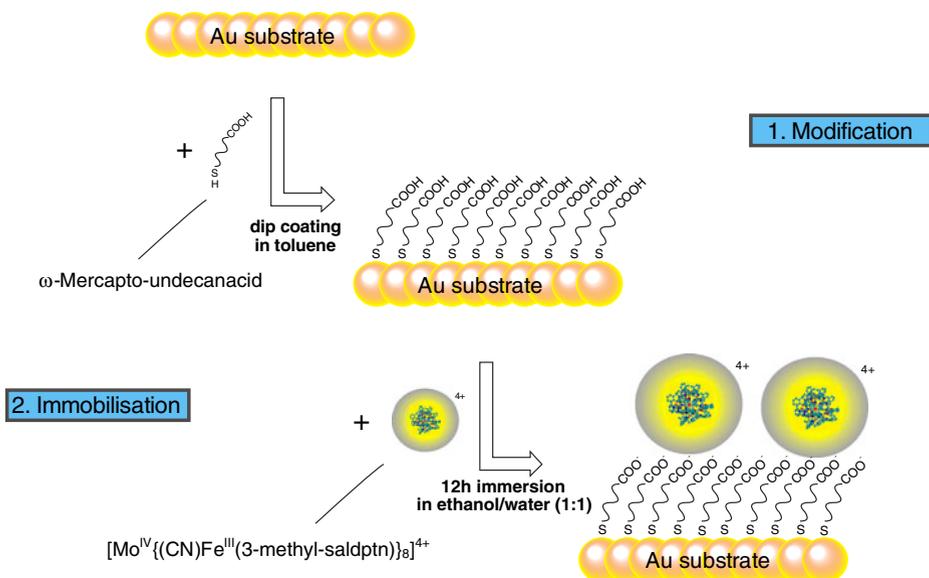


Fig. 2 Graphical representation of the immobilisation of $[\text{Mo}^{\text{IV}}\{(\text{CN})\text{Fe}^{\text{III}}(3\text{-methyl-saldptn})\}_8]\text{Cl}_4$ **1** using a self-assembled monolayer

In this contribution the effect of the immobilisation on the nonanuclear spin crossover compound is demonstrated by direct comparison of bulk and surface Mössbauer spectroscopic measurements.

2 Experimental

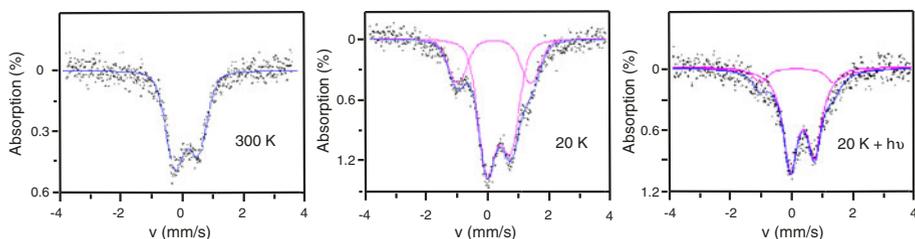
2.1 Nonanuclear complex **1**

$[\text{Mo}^{\text{IV}}\{(\text{CN})\text{Fe}^{\text{III}}(3\text{-methyl-saldptn})\}_8]\text{Cl}_4$ was synthesized as described in [12].

2.2 Immobilisation of $[\text{Mo}^{\text{IV}}\{(\text{CN})\text{Fe}^{\text{III}}(3\text{-methyl-saldptn})\}_8]\text{Cl}_4$ onto a gold surface

The immobilisation results from electrostatic interactions between a modified and therefore negatively charged gold surface and the four-times positively charged complex (Fig. 2).

The gold surface is prepared by deposition of a 50 nm gold layer at a freshly cleaved mica slide. Onto this substrate a monolayer of ω -mercapto-undecanoic acid is deposited by a dip coating process in toluene. After cleaning the slides with 2-propanol, the clusters are bound ionically by a dip coating process as well: A solution of 10 mg $[\text{Mo}^{\text{IV}}\{(\text{CN})\text{Fe}^{\text{III}}(3\text{-methyl-saldptn})\}_8]\text{Cl}_4$ dissolved in 20 mL of an ethanol/water mixture in a 1:1 ratio is prepared. The carboxylic acid modified gold surface is immersed in this solution for 12 h. Afterwards the slides are washed with 2-propanol three times. To remove the clusters from the surface an aqueous 0.1 molar CaCl_2 solution can be used.



| | 300 K | | | 20 K | | | | | |
|--------------------|--------|------|------|--------|------|------|--------|------|------|
| Surface bound | Site 1 | | | Site 1 | | | Site 2 | | |
| | Pop[%] | IS | QS | Pop[%] | IS | QS | Pop[%] | IS | QS |
| 1 | 100 | 0.35 | 0.82 | 72 | 0.47 | 0.81 | 28 | 0.31 | 2.45 |
| 1 + hv | | | | 85 | 0.47 | 0.80 | 14.8 | 0.28 | 2.45 |
| Bulk material [11] | Site 1 | | | Site 1 | | | Site 2 | | |
| | Pop[%] | IS | QS | Pop[%] | IS | QS | Pop[%] | IS | QS |
| 1 | 100 | 0.35 | 0.82 | 83 | 0.48 | 0.80 | 17 | 0.26 | 2.5 |

Fig. 3 Mössbauer spectra of immobilised $[\text{Mo}^{\text{IV}}\{(\text{CN})\text{Fe}^{\text{III}}(3\text{-methyl-saldptn})\}_8]\text{Cl}_4$ clusters on Au(111) surfaces using a self-assembled monolayer

3 Results and discussion

Mössbauer measurements were performed in transmission and reflection geometry using a constant acceleration spectrometer and a helium bath cryostat. ^{57}Fe Mössbauer spectra were recorded between room temperature and 20 K using the 50 mCi source $^{57}\text{Co}(\text{Rh})$. The RECOIL 1.03 Mössbauer Analysis Software was used to fit the experimental spectra [14]. Isomeric shift values are quoted relative to $\alpha\text{-Fe}$ at 293 K.

The measurements indicate that the spin crossover was maintained: Fig. 3 shows the temperature-dependent Mössbauer spectra of the nonanuclear compound **1** bound to a gold surface. As expected the measurements in reflection geometry show a less intensity in comparison to the bulk measurements [11]. In the Mössbauer spectrum at 300 K a quadrupole splitted doublet is observed which is slightly broadened due to relaxation, common for Fe(III) in its HS state ($S = 5/2$) [9, 10]. At 20 K the Mössbauer spectrum shows in addition to the Fe(III) in the HS state a second doublet which is characteristic for a Fe(III) in the LS state [9, 10]. A light irradiation ($25 \text{ mW}/\text{cm}^2$, 514.5 nm green argon ion laser) at 20 K significantly alters the population of both states reversibly. Hence, the nonanuclear compound did not lose its thermal and optical “switchability” during the immobilisation to the gold surface. At 20 K the LS state is altered by ca. 11%, which is remarkably small with respect to a matrix and an anion exchange from chloride to carboxylate. **1** clearly exhibits after the immobilisation a thermally induced spin transition between HS and LS state. The area fraction of the respective doublets $A(\text{Fe}^{\text{III}}\text{-HS})$: $A(\text{Fe}^{\text{III}}\text{-LS})$ indicates that several Fe(III) centres switch. Therefore, there is a multiple electronic transition.

These results indicate that a surface bound cluster of **1** still bears the potential to act as a switch. Furthermore, those findings emphasize the possibility of fabricating

molecule based low-dimensional structures of spin crossover compounds by using self-assembled monolayers.

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