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Exposure of $[Mn^{III}_6Cr^{III}]^{3+}$ single-molecule magnets to soft X-rays: The effect of the counterions on radiation stability

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ABSTRACT

X-ray absorption spectroscopy studies of the $[Mn^{III}_6Cr^{III}]^{3+}$ single-molecule magnet deposited as a microcrystalline layer on gold substrates are presented. The oxidation state of the manganese centers changes from Mn^{III} to Mn^{II} due to irradiation with soft X-rays. The influence of the charge-neutralizing anions on the stability of $[Mn^{III}_6Cr^{III}]^{3+}$ against soft X-ray exposure is investigated for the different anions tetraphenylborate (BPh_4^-), lactate ($C_3H_5O_3^-$) and perchlorate (ClO_4^-). The exposure dependence of the radiation-induced reduction process is compared for $[Mn^{III}_6Cr^{III}]^{3+}$ with the three different anions.

1. Introduction

With the ongoing development of technology towards smaller devices and structures, more and more efforts are made to assign specific tasks to single molecules. In this context, the so-called single-molecule magnets (SMM) are a promising approach [1]. Single-molecule magnets represent a class of coordination compounds which exhibit a magnetic bistability [2–4]. At low temperatures the existence of an energy barrier for spin reversal leads to a slow relaxation of the magnetization [5,6]. It was recently shown that single-molecule magnets grafted to surfaces do not lose their magnetic properties [7]. This represents an important step towards practical applications of SMM. For Fe_4 complexes [8], a preferential orientation on Au surfaces could be established by chemical means. 3D nanostructures consisting of single-molecule magnets are also being investigated [9].

We have developed the single-molecule magnet $[\{(talen^{t\text{-}Bu_2})Mn^{III}_3\}_2\{Cr^{III}(CN)_6\}]^{3+}$ ($[Mn^{III}_6Cr^{III}]^{3+}$) with $H_6talen^{t\text{-}Bu_2}$ {= 2, 4, 6-tris{1-[2-(3, 5-di-*tert*-butylsalicylaldimino)-2-methylpropylimino]−ethyl}-1, 3, 5-trihydroxybenzene} [10,11]. This molecule contains six Mn^{III} ions arranged in two bowl-shaped trinuclear triplesalen building blocks which are linked by a hexacyanochromate (see Fig. 1). The strongest interaction is the antiferromagnetic coupling of the central Cr^{III} ion with the six terminal Mn^{III} ions, leading to a large spin ground state of $S_t = 21/2$ for the molecule. This high spin ground state in combination with a strong easy-axis magnetic anisotropy and a C_3 symmetry results in an energy barrier for spin-reversal and thus in a slow relaxation of the magnetization at low temperatures. The $[Mn^{III}_6Cr^{III}]^{3+}$ complex can be isolated with different anions which compensate for its triply positive charge. Recently, first results from spin-resolved electron spectroscopy of the manganese centers in $[Mn^{III}_6Cr^{III}]^{3+}$ have been presented and compared to data from reference substances [12]. In the work presented here, the three salts $[Mn^{III}_6Cr^{III}](BPh_4)_3$, $[Mn^{III}_6Cr^{III}](C_3H_5O_3)_3$, and $[Mn^{III}_6Cr^{III}](ClO_4)_3$ using either tetraphenylborate (BPh_4^-), lactate ($C_3H_5O_3^-$) or perchlorate (ClO_4^-) as anions, respectively, were investigated by L-edge X-ray absorption spectroscopy deposited on surfaces.

The investigation of metal-organic compounds containing transition metal centers within an organic ligand structure by

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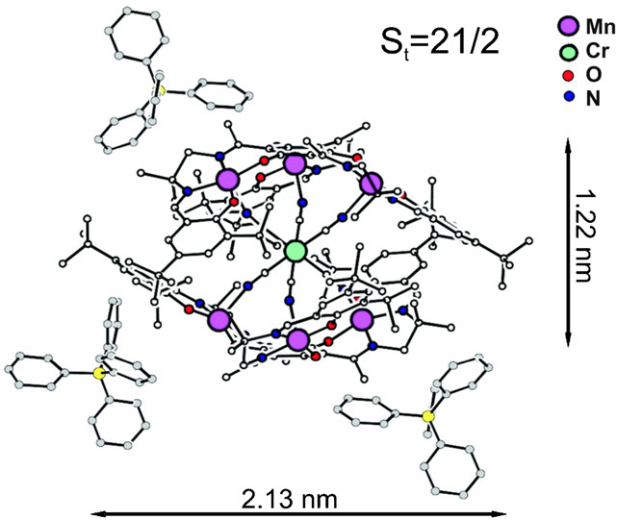

Fig. 1. Molecular structure of $[Mn^{III}_6Cr^{III}]^{3+}$ in crystals of $[Mn^{III}_6Cr^{III}](BPh_4)_3$•4MeCN•2Et$_2$O. The two bowl-shaped triplesalen building blocks each containing three Mn^{III} ions (magenta) are linked by a hexacyanochromate containing a Cr^{III} ion (cyan) [10]. Also shown are the three tetraphenylborate (BPh_4^-) anions.

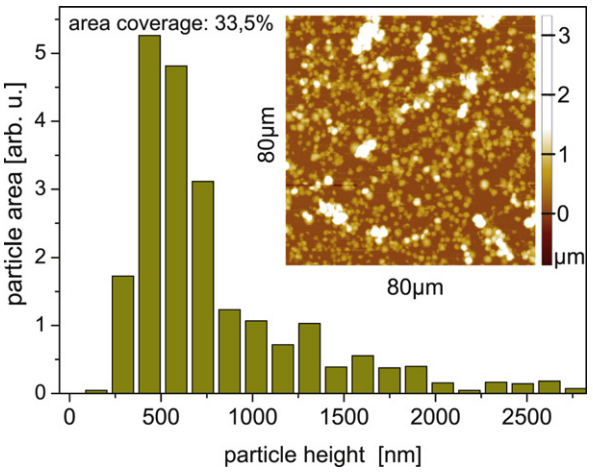

Fig. 2. Particle height distribution in a 80 µm by 80 µm area of a $[Mn^{III}_6Cr^{III}](ClO_4)_3$ microcrystallite sample, derived from the AFM scan shown in the inset.

X-ray-based methods is mostly complicated by the occurrence of radiation damage [13,14]. These damage effects are also well known in protein crystallography [15] using hard X-rays and are possibly caused by the large number of electrons photoexcited in the sample upon irradiation [16]. Radiation damage related to soft X-ray exposure exists also for the $[Mn^{III}_6Cr^{III}]^{3+}$ single-molecular magnets presented here – it is indicated by the reduction of the Mn^{III} metal centers in the SMM to the Mn^{II} oxidation state. The extent of the radiation-induced reduction strongly depends on the choice of anions, which is described in detail below.

2. Sample preparation

$H_6talen^{t\text{-}Bu_2}$ {= 2, 4, 6-tris{1-[2-(3, 5-di-*tert*-butylsalicylaldi − mino)-2-methylpropylimino] − ethyl}-1, 3, 5-trihydroxybenzene} and $[\{(talen^{t\text{-}Bu_2})Mn^{III}\}_2\{Cr^{III}(CN)_6\}(MeOH)_3(MeCN)_2](BPh_4)_3$• 4MeCN•2Et$_2$O (abbrev. $[Mn^{III}_6Cr^{III}](BPh_4)_3$) were synthesized as described previously [10,17,18]. The perchlorate salt (abbrev. $[Mn^{III}_6Cr^{III}](ClO_4)_3$) was synthesized according to the following procedure described in detail below. $[\{(talen^{t-Bu_2})(Mn^{III}(MeOH))_3\}_2\{Cr^{III}(CN)_6\}](ClO_4)_3$. A suspension of $H_6talen^{t\text{-}Bu_2}$ (550 mg, 0.495 mmol) and $Mn(OAc)_2$•4H$_2$O (343 mg, 1.40 mmol) in methanol (200 mL) was heated at reflux for 2 h. The resulting brown solution was cooled to room temperature, purged with air for 30 min and heated at reflux for additional 2 h. After cooling to room temperature the reaction solution was treated with a solution of $K_3[Cr(CN)_6]$ (81 mg, 0.25 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 60 min and filtered. A solution of $NaClO_4$•H$_2$O (1645 mg, 11.71 mmol) in methanol (40 mL) was added to the filtrate. The reaction mixture was stirred at room temperature for 10 min and filtered again. Stirring of the filtrate for 16 h at room temperature resulted in the formation of a brown precipitate, which was collected by filtration and dried in vacuo. The resulting brown powder was dissolved in methanol. Slow diffusion of diethyl ether into the solution afforded large black crystals. Yield: 223 mg (28%). ESI-MS (MeCN): *m/z*: 915.9 $[\{(talen^{t\text{-}Bu_2})Mn_3\}_2\{Cr(CN)_6\}]^{3+}$, 1374.2 $[\{(talen^{t\text{-}Bu_2})Mn_3\}_2\{Cr(CN)_6\}]^{2+}$, 2747.2 $[\{(talen^{t\text{-}Bu_2})Mn_3\}_2\{Cr(CN)_6\}]^{+}$; MALDI-TOF-MS (matrix DCTB): *m/z*: 2946.5 $\{[\{(talen^{t\text{-}Bu_2})Mn_3\}_2\{Cr(CN)_6\}](ClO_4)_2\}^{+}$, 2846.9 $\{[\{(talen^{t\text{-}Bu_2})Mn_3\}_2\{Cr(CN)_6\}]ClO_4\}^{+}$, 2746.4 $[\{(talen^{t\text{-}Bu_2})Mn_3\}_2\{Cr(CN)_6\}]^{+}$; IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2957m, 2907m, 2870m, 2156w, 1613s, 1567s, 1539s, 1493vs, 1437m, 1395m, 1363m, 1339m, 1310m, 1275s, 1254s, 1188m, 1153m, 1142m, 1121m, 1090m, 1063m, 1026w, 845m, 820w, 779w, 750w, 642w, 625w, 608w, 575m, 552m. Elemental analysis (%): calcd for $C_{150}H_{216}N_{18}O_{30}Cl_3CrMn_6$: C 55.62, H 6.72, N 7.78; found: C 55.49, H 6.64, N 7.87.

$[\{(talen^{t-Bu_2})(Mn^{III}(MeOH))_3\}_2\{Cr^{III}(CN)_6\}](C_3H_5O_3)_3$•9MeOH was prepared similarly using D,L-$C_3H_5O_3Na$ instead of $NaClO_4$•H$_2$O. The resulting substance is abbreviated as $[Mn^{III}_6Cr^{III}](C_3H_5O_3)_3$ in this publication. Further details will be published in a forthcoming article.

Crystalline batches of the $[Mn^{III}_6Cr^{III}]^{3+}$ salts were checked by X-ray diffraction (XRD) and infrared spectroscopy (see above) with regard to their desired chemical and physical properties. Solutions of the $[Mn^{III}_6Cr^{III}]^{3+}$ salts with a concentration of 4.5×10^{-4} mol/l were prepared by dissolving the compounds in methanol.

For the measurements presented here, 10 µl of the methanolic solutions of $[Mn^{III}_6Cr^{III}](BPh_4)_3$ and $[Mn^{III}_6Cr^{III}](ClO_4)_3$ were dripped on horizontally oriented square substrates with an edge length of 5.5 ± 1.0 mm. For $[Mn^{III}_6Cr^{III}](ClO_4)_3$ microcrystallites began to grow in the liquid phase during solvent evaporation and to form a granular deposit on the substrate surface. The particle heights vary between 250 nm and 3000 nm, a large fraction of the microcrystallites show a height of 500 ± 250 nm (see Fig. 2). The area coverage is about 30%.

By optical microscopy the $[Mn^{III}_6Cr^{III}](BPh_4)_3$ sample reveals a closed deposit layer with only small, irregular aggregations of microcrystallites on top. The abundance of microcrystallites is much lower than for $[Mn^{III}_6Cr^{III}](ClO_4)_3$ and increases towards the sample edges. Particle sizes are comparable to those found for the SMM samples with perchlorate anions.

The methanolic solution of $[Mn^{III}_6Cr^{III}](C_3H_5O_3)_3$ shows a completely different wetting behaviour: No optically discernible crystallites form in this case, but a plain deposit layer without recognizable structures instead. Only 5 µl of this solution was necessary to form a complete layer.

All SMM samples prepared as described reveal a border area consisting of macroscopic deposits near the substrate edges. The substrates used for our investigations are commercially available[1]

[1] Brand name: Arrandee, Manufacturer: Dr. Dirk Schröer, Schlossstrasse 94, D-33824 Werther, Germany.