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Spin Crossover in a Tetranuclear Cr(III)–Fe(III)$_3$ Complex

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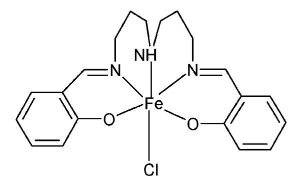
A novel heteronuclear exchange-coupled complex $[Cr^{III}\{(CN)Fe^{III}(^5L)\}_3(CN)_3]$ containing a pentadentate blocking ligand ^{5}L was synthesized. The X-ray structure shows that a meridional isomer applies with inequivalent Fe^{III} centers. The complex exhibits a thermally induced spin crossover along with the exchange coupling. Mössbauer spectra indicate a spin transition between $S = {}^1/_2$ and $S = {}^5/_2$ states although a considerable amount of Fe^{III} centers stays high-spin at $T = 6$ K. The magnetization, the magnetic susceptibility, and the Mössbauer data were fitted in one run with a spin crossover model taking into account exchange interactions among all metal centers.

One of the strategies in preparing polynuclear complexes is to utilize some building blocks $[M(^nL)X_m]$ which possess several sites occupied by a suitable multidentate ligand ^{n}L and one or two labile M−X bonds. The labile bond could be replaced when the precursor is combined with a multi-finger central block like $[M(CN)_6]$.[1] The need of preparing polynuclear complexes exhibiting a large-spin ground state is strongly motivated by the target to synthesize molecule-based and single-molecule magnets.[2]

$^5LH_2$ = (*saldpt*)H$_2$ = *N,N′*-bis(1-hydroxy-2-benzylidene)-1,7-diamino-4-azaheptane represents one of the candidates to function as a pentadentate blocking ligand. The complex $[Fe^{III}(^5L)Cl]$ (see Chart 1) is high-spin, $S = {}^5/_2$ (its X-ray structure is reported elsewhere),[3] but the pyridine complex $[Fe^{III}(^5L)(py)]Cl$ exhibits a thermally induced spin crossover from $S = {}^1/_2$ to $S = {}^5/_2$ states.[4] The binuclear complex $[\{Fe^{III}(^5L)\}_2(4,4'\text{-bipy})]^{2+}$ bridged by the 4,4′-bipyridine exhibits spin crossover as well crossing the room temperature region.[5] The manifoldness of the spin crossover in Fe^{III} complexes with low-symmetry coordination sphere is that besides $S = {}^1/_2$ to ${}^5/_2$ also ${}^1/_2$ to ${}^3/_2$ and ${}^3/_2$ to ${}^5/_2$ spin transitions were observed.[6] The *saldpt* ligand itself is a promising candidate of stabilizing a great variety of spin states, depending upon the coligand in the closing position of the coordination sphere and the counterions in the solid state.

Chart 1. Structure of the Precursor [Fe(*saldpt*)Cl]



Copper(II) and cobalt(II) complexes of its methyl substituent (*saldptm*) have been well characterized elsewhere.[7] There are reports on $S = 15$ ground state in the complexes $[Fe^{II}(CN)_6\{Fe^{III}(saldptm)\}_6]Cl_2$•solvent.[8] On the contrary, the complexes of $[Fe^{II}(CN)_6\{Fe^{III}(saldpt)\}_6]X_2$ (X = Cl, BPh$_4$) possess the $S = 0$ ground state with a very small bandwidth owing to which many magnetically productive excited states are thermally populated at $T = 4.2$ K and higher so that the magnetic susceptibility and magnetization follow an effective $S = 6$ state.[9]

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We report herein about the structural and magnetic properties of a novel molecular complex compound $[(NC)_3Cr^{III}\{CNFe^{III}(saldpt)\}_3]$, **1**.

The pentadentate ligand has been prepared by a Schiff base condensation: a mixture of the salicylaldehyde (0.2 mol) and 1,7-diamino-4-azaheptane (0.1 mol) in methanol (100 cm^3) was boiled for 10 min, and the solution was subjected to crowding. The yellow oily material, $(saldpt)H_2$, resulted, and NMR spectra agree with the expected structure.

The precursor [Fe(*saldpt*)Cl] has been prepared from a solution of anhydrous $FeCl_3$ (10 mmol) in methanol (50 cm^3) added to a solution of $(saldpt)H_2$ (10 mmol) in methanol (40 cm^3). The mixture was stirred at 50 °C for 10 min, and then triethylamine (22 mmol) was added. The resulting solution was stirred at 50 °C for 1 h, and after cooling black crystals precipitated. These were washed with methanol and diethyl ether and dried in a vacuum. Elemental analysis calcd (%) for $C_{20}H_{23}N_3ClFeO_2$: C 56.0, H 5.41, N 9.80, Fe 13.0, Cl 8.27; found C 55.7, H 5.38, N 9.84, Fe 13.1, Cl 8.22.

The tetranuclear complex $[(NC)_3Cr^{III}\{CNFe^{III}(saldpt)\}_3]$ has been obtained from a methanol solution (50 cm^3) of [Fe(*saldpt*)Cl] (1 mmol) combined with a water−methanol solution of $K_3[Cr(CN)_6]\cdot 2H_2O$ (0.160 mmol). In 2 days dark crystals were separated, washed with methanol and diethyl ether, and dried under nitrogen atmosphere. Yield: 0.12 g (55%). Elemental analysis calcd (%) for $C_{66}H_{69}N_{15}O_6CrFe_3$: C 57.1, H 5.01, N 15.1, Fe 12.1; found C 54.5, H 4.82, N 14.8, Fe 11.8. (Lowered C- and N-content is ascribed to the formation of stable carbides and nitrides when cyanides burn in a commercial C−H−N analyzer.) Single crystals were grained to a fine powder used in physical measurements.[10]

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(10) An ac susceptometer/magnetometer (LakeShore, model 7225) was used in magnetization and susceptibility measurements (field parameters: $f = 222\ s^{-1}$, $H_{ac} = H_{dc} = 800\ A\ m^{-1}$; correction to the underlying diamagnetism with Pascal constants). A conventional Mössbauer spectrometer setup equipped with an He-flow cryostat was used (4.2−300 K). A $^{57}Co/Rh$ source was used, kept at room temperature (calibration to α-Fe at room temperature, units are in mm s^{-1}). A single crystal of **1** was mounted to a four-circle diffractometer (Nonius KappaCCD, λ(Mo Kα) = 0.71069 Å, graphite monochromator). Crystal data for $C_{66}H_{69}CrFe_3N_{15}O_6$ at $T = 183$ K: triclinic, space group $P\bar{1}$ (No. 2), $a = 13.792(8)$ Å, $b = 17.771(11)$ Å, $c = 17.835(9)$ Å, $\alpha = 102.36(2)°$, $\beta = 106.39(3)°$, $\gamma = 106.13(4)°$, $V = 3820(2)$ $Å^3$, $Z = 2$, $\rho_{calcd} = 1.204\ g\ cm^{-3}$, μ(Mo Kα) = 0.751 mm^{-1}; 3146 reflections were measured ($0 \leq h \leq 10$, $-13 \leq k \leq 12$, $-13 \leq l \leq 12$, $2.94° \leq \theta \leq 15.48°$) of which 2193 were independent, and 1632 independent for $I > 2\sigma(I)$. Structure solution: direct methods with SHELXS-97; refinement (parameters/restraints = 491/24) with SHELXL-97; empirical absorption correction with SORTAV.[11] Refinement of F^2 against all 2193 reflections; $wR(F^2) = 0.3900$, $S(F^2) = 1.750$, $R(F) = 0.1686$ with F set to zero for negative F^2; residual density 1.61/−0.63 $eÅ^{-3}$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used for calculating R-factors ($wR_{gt} = 0.3562$, $R_{gt} = 0.1367$) but not to the choice of reflections for refinement. The refinement is far from being perfect, because of poor quality of the crystal with low diffraction power resulting from high mosaicity (2.5°). Moreover, at $T = 183$ K both, low-spin and the high-spin centers coexist, and these refer to different Fe−N separations. Thus the results of the X-ray structure analysis serve for confirmation of the structure motif and determination of a molar mass for **1**.

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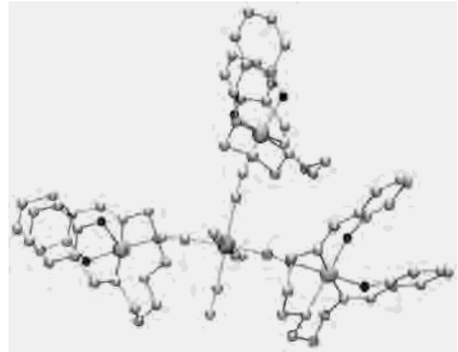

Figure 1. X-ray structure of **1** (hydrogen atoms omitted for clarity).

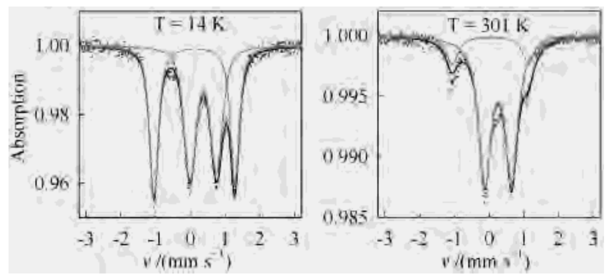

Figure 2. Representative Mössbauer spectra of **1**.

X-ray structure analysis shows that the prepared tetranuclear complex possesses the molecular structure: the central Cr^{III} atom is coordinated by six carbon atoms from the CN^- ligands; three $\{Fe^{III}(saldpt)\}^+$ units are further coordinated to the nitrogen atoms bearing thus a bridging functionality (Figure 1). The meridional arrangement is adopted. The important interatomic distances (Å) are as follows: $Cr-CN_{terminal} = 1.79(5)_{trans}$, $1.94(5)_{cis}$, $1.99(4)_{trans}$; $Cr-CN_{bridge} = 2.02(3)_{trans}$, $2.15(4)_{cis}$, $2.06(3)_{trans}$; $Fe-NC_{bridge} = 2.19(3)_{trans}$, $1.96(3)_{cis}$, $2.08(3)_{trans}$.

The Mössbauer spectra (Figure 2 and Supporting Information) show two different kinds of the coexisting Fe^{III} centers whose ratio alters with temperature in favor of the high-spin states. The first doublet possesses $\delta = 0.1$ and $E_Q = 2.3$ characteristic for Fe^{III} in the $S = {}^1/_2$ state at the octahedral geometry.[12] The second doublet with $\delta = 0.3$ and $E_Q = 0.7$ refers to Fe^{III} in the $S = {}^5/_2$ state. This HS state doublet shows small asymmetry which can be assigned to distribution, as indicated by X-ray structure data. The deconvoluted area fractions show that at $T = 14$ K the high-spin mole fraction is still considerable: $x_{HS} = A_H/(A_H + A_L) = 0.53$ as seen in Figure 3.

The magnetic susceptibility on cooling increases; its inverse shows an overall ferromagnetic deviation from linearity at low temperature. The effective magnetic moment for **1** gradually decreases on cooling from the value of $\mu_{eff} = 9.0\ \mu_B$ at $T = 300$ K to the value of $\mu_{eff} = 6.5\ \mu_B$ at $T = 5$ K (Figure 3). There seems to be a plateau at ca. 10 K, with a second one around 100 K. The field dependence of the magnetization shows that the saturation limit overreaches the value of $M_{mol}/N_A = 3.0\ \mu_B$ for a single Cr^{III} center.

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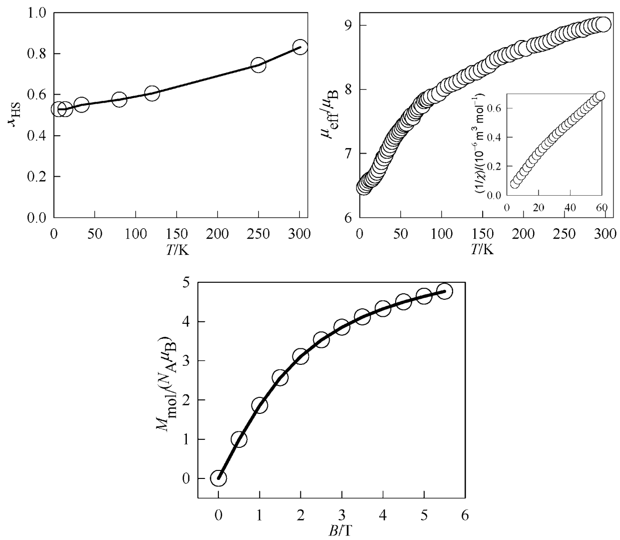

Figure 3. Mössbauer-data high-spin mole fraction (top left), temperature dependence of the effective magnetic moment (top right), and field dependence of the magnetization at $T = 4.5$ K (bottom). Solid lines: guide for the eye.

For the involvement of the exchange interaction, four reference states are to be considered, i.e., LLL, HLL, HHL, and HHH where L is the low-spin and H is the high-spin center of Fe^{III}. All these states can be characterized by a common spin Hamiltonian involving the isotropic exchange and the Zeeman term

$$\hat{H}^{spin} = \hbar^{-2}[-J_1(\vec{S}_{Cr}\cdot\vec{S}_{Fe1}) - J_2(\vec{S}_{Cr}\cdot\vec{S}_{Fe2}) - J_3(\vec{S}_{Cr}\cdot\vec{S}_{Fe3})] + \mu_B B\hbar^{-1}(g_{Cr}\vec{S}_{Cr} + g_{Fe1}\vec{S}_{Fe1} + g_{Fe2}\vec{S}_{Fe2} + g_{Fe3}\vec{S}_{Fe3})$$

Using $g_{Cr} = g_{Fe(HS)} = 2.0$ we are left with three free parameters $J_L(Cr-Fe_{LS})$, $J_H(Cr-Fe_{HS})$, and $g_L(Fe_{LS})$.

The evaluation of the matrix elements, energy levels, and the magnetic functions for exchange coupled clusters is described elsewhere.[13] Each of these states forms an energy band: 32 levels for $S_{LLL} \in \langle 0, 3\rangle$, 96 levels for $S_{HLL} \in \langle 0, 5\rangle$, 288 levels for $S_{HHL} \in \langle 0, 7\rangle$, and 864 levels for $S_{HHH} \in \langle 0, 9\rangle$. The barycenters of these bands are separated by a gap of Δ_1(HLL−LLL), Δ_2(HHL−HLL), and Δ_3(HHH−HHL), respectively. The isotropic exchange Hamiltonian is incapable of determining these relative positions.

There are two supporting pieces of external information: (i) the magnetization data show that not only the LLL is present at $T = 4.5$ K; (ii) the Mössbauer data show a presence of ca. 50% the local high-spin state at this temperature. Of several hypotheses two models were tested numerically: (i) A model which comprises two sublattices was tested. In the first one, there are all iron centers in the high-spin state. In the second sublattice, the molecules undergo a three-center spin crossover with temperature LLL → HLL → HHL → HHH (the assumption of two sublattices is quite common in treating systems with incomplete quenching of the spin crossover at low temperature); (ii) HLL and HHL coexist at low temperature (then Δ_1 is very negative and Δ_2 small) and undergo the spin crossover HLL → HHL → HHH.

In order to characterize the spin crossover,[14] the Ising-like model was extended to the three-center case (Supporting Information). Notice, the spin-crossover parameters (Δ_1, Δ_2, Δ_3, the effective degeneracy ratio r_{eff}, and the intermolecular cooperativeness j) are independent of the magnetic exchange and they could be fixed on the Mössbauer data alone. A very gradual spin transition x_{HS} vs T is assigned to the Boltzmann distribution among LLL, LLH, LHH, and HHH reference states which disfavors a complete transition to the HHH entities. Some more recent data on dinuclear and polynuclear complexes show that the spin crossover in them could be much more gradual than in the mononuclear counterparts; a broad plateau is a characteristic feature of them.[15] Three sets of experimental data (Mössbauer data, susceptibility, and magnetization) were fitted simultaneously yielding $J_L/hc = +16.4$ cm^{-1}, $J_H/hc = -11.0$ cm^{-1}, $g_L = 2.39$, $\Delta_2/k = 46$ K, $\Delta_3/k = 172$ K.[16] For Δ_1 negative enough the LLL state is lifted above the accessible thermal population and the first transition step does not occur; only the first plateau, the second step, the second plateau, and the third step can be seen.

In conclusion, the synthesized tetranuclear complex $[(NC)_3Cr^{III}\{CNFe^{III}(saldpt)\}_3]$ is the first T-shaped structured spin crossover system as characterized by the X-ray structure analysis, Mössbauer spectra, magnetization, and magnetic susceptibility measurements. A heterometallic cyanide-bridged compound with magnetic exchange interplays with a spin transition.

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Supporting Information Available: Structure data (atom labeling, interatomic distances), Mössbauer spectra, details on the derivation of the spin crossover model, and data fitting. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The full list of free parameters covers the magnetic exchange (J_H, J_L, and g_L) and the three-center spin crossover model (Δ_1, Δ_2, Δ_3, r_{eff}, j). Their reliable determination is an ambitious task, and it could be done only when three primary experimental data sets are treated simultaneously: the magnetization (an increasing curve), the magnetic susceptibility (a decreasing curve), and the high-spin mole fraction (a sigmoidal-type curve). Therefore a common functional has been constructed and minimized using nonlinear optimization techniques (genetic algorithms with 10^6 searches).