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Filling the Gap in the Metallacrown Family: The 9-MC-3 Chromium Metallacrown

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Abstract: In this work, we report on a long-sought missing complex in the metallacrown family. We synthesized and characterized the novel chromium metallacrown (MC) complex $\{\text{Cr}^{\text{III}}(\mu_2\text{-piv})_3[9\text{-MC}_{\text{Cr}^{\text{III}}(\text{sh}^3-)}\text{-3}](\text{morph})_3\} \cdot \text{MeOH}$ (in which $\text{sh}^3- = \text{salicyl hydroxamate}$, $\text{piv} = \text{pivalate}$, and $\text{morph} = \text{morpholine}$). The MC with a 9-MC-3 cavity of kinetically inert chromium(III) ions was synthesized by a solvothermal reaction. Magnetization measurements reveal a high spin ground state.

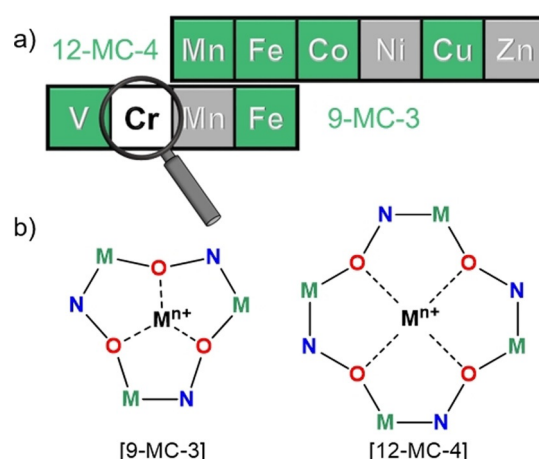
Metallacrowns (MCs) belong to a continuously developing class of compounds in the field of molecular recognition,^[1–4] catalysis,^[5] and magneto chemistry.^[6–10] Like their organic crown ether analogs, MCs contain oxygen donor atoms in their repeating units, $-\text{[M-N-O]}_n-$, allowing them to coordinate metal guest ions. This makes them perfect candidates for molecular recognition.^[1]

The very first metallacrowns, which were reported by V. Pecoraro in 1989, included the complexes $[(\text{VO})_3(\text{sh}^3-)_3(\text{CH}_3\text{OH})_3]^{[12]}$ and $[\text{Fe}_4(\text{sh}^3-)_3(\text{MeOH})_3(\text{OAc})_3]^{[13]}$. Both showed a 9-MC-3 structural motif. While vanadium 9-MC-3 was vacant and therefore had no guest ion,^[12] the iron complex contained iron(III) as the central guest ion (Scheme 1). Thus, Pecoraro et al. forecasted more than 30 years ago that „[...] it should be possible to form [...] metallacrown ethers through synthesis of the kinetically inert Co^{III} or Cr^{III} analogues. We expect that these exchange inert clusters will form the 9-C-3 structure since the metals should be octahedral.“^[13] While we reported the first cobalt MC with a 12-MC-4 cavity in 2015,^[9] no chromium metallacrown with either a classical 12-MC-4 or a 9-MC-3 motif has been reported in the last 30 years. Now, we

have filled this gap in the metallacrown family by synthesizing the first 9-MC-3 chromium(III) complex.

The likely reason for the absence of Cr-MCs is due to the challenging chemistry of chromium(III). Cr^{3+} is a kinetically inert metal ion that requires thermodynamically well-suited reaction conditions.^[14] One possibility is working under basic conditions to deprotonate the desired ligands and facilitate their ligation. However, oxido-complexes are easily formed, even if the precipitation of $\text{Cr}(\text{OH})_x$ is avoided by controlling the pH.^[15,16] Indeed, μ_3 -oxo-bridged trinuclear metal carboxylates $[\text{Cr}^{\text{III}}(\mu_3\text{-O})(\text{RCOO})_6\text{L}_3]^+$ are well known in literature.^[17] Although few complexes with additional bridging μ_2 -oxime ligands are found in literature, no reports on Cr-based MCs exist.^[18,19] We attribute this lack to synthetic challenges. Fortunately, solvothermal reaction conditions have now paved the way for the synthesis of chromium(III) MCs. By applying moderate pressure and high temperatures, we were able to obtain the 9-Cr-3 MC.

Our research focuses on the magneto chemistry of MCs. In recent years, MCs have proven that they can behave as Single-Molecule Magnets, SMMs.^[7,23,25] The use of kinetically inert metal ions can increase the stability of MCs which is necessary to enable the processing of MC-based SMMs.^[26] We herein report the first step towards this goal. The enhanced stability will open the field for heterometallic MCs using kinetic inert ring-building Cr^{3+} on the one hand and embed magnetic ani-



Scheme 1. a) Color code: green: elements for which classical MCs with shi are reported,^[1,9] gray: For Ni,^[20,21] Zn,^[22] and Mn^[23,24] ions (the latter in 9-MC-3), MCs with various other ligands are reported; b) schematic representation of the repetition units for a [12-MC-4] and a [9-MC-3] cavity with guest metal ions (black color).

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sotropic guest ions achieving SMM behavior on the other hand.

$\{\text{Cr}^{\text{III}}(\mu_2\text{-piv})_3[9\text{-MC}_{\text{Cr}(\text{III})\text{N}(\text{shi})^{-3}}](\text{morph})_3\}\cdot\text{MeOH}$, hereafter referred to as $[\text{Cr}_3\text{Cr}]\text{-MC}$ crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The crystallographic data as well as selected bond lengths and angles are summarized in the SI (Table S1–S4, Deposition numbers 2047296 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service). As the basic reaction conditions facilitate the full deprotonation of the ligand, three salicylhydroxamtes, shi^{3-} , coordinate the chromium(III) ring metal ions Cr1, Cr2, and Cr3, and form a 9-MC-3 cavity with the characteristic repetition unit $[\text{Cr-N-O}]$ (see Figure 1).

All chromium (III) ions are octahedrally coordinated, as expected based on their d^3 electronic configuration (see Figure S5). For the ring-forming metal ions, this means that the shi^{3-} ligands are coordinated, providing four donor atoms (three O-donor atoms and one N-donor atom). An N-donor atom from a morpholine co-ligand and an O-donor atom from a pivalate complete the octahedral coordination (Figure 2 b).

As the ligands are oriented *cis* to each other, the metal ions adopt an asymmetric *cis*-propeller configuration. This chiral arrangement can lead to two different isomers. Only the right-handed Δ -isomer is shown in Figure 2. It is important to note that the same chirality for all ring metal ions is a prerequisite for forming a 9-MC-3 with the repetition unit $[\text{Cr-N-O}]$. Hence, all ring metal ions must have either $\Delta\Delta\Delta$ or $\Lambda\Lambda\Lambda$ chirality (Figure 2 and S4). Figure 1 depicts the $\Delta\Delta\Delta$ - Δ isomer of the $[\text{Cr}_3\text{Cr}]\text{-MC}$. Due to the centrosymmetric space group, a racemate with the Δ -isomer and Λ -isomer naturally results in a solid-state, as shown in Figures S4 and S5. For detailed information on the determination of chirality, see Supporting Information.

Finally, it is worth noting that the small cavity of the 9-MC-3 ring does not allow coordination of the central chromium ion in the center. This leads to considerable out-of-plane coordination of Cr4. The guest ion is located 1.89 Å above the Cr1, Cr2,

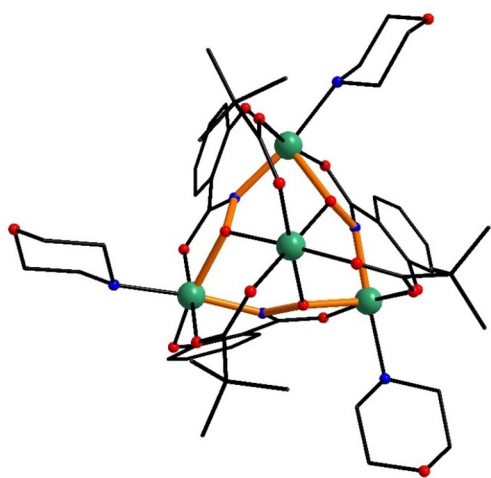


Figure 1. Schematic representation of the molecular structure of $\text{Cr}^{\text{III}}(\mu_2\text{-piv})_3[9\text{-MC}_{\text{Cr}(\text{III})\text{N}(\text{shi})^{-3}}](\text{morph})_3$. Hydrogen atoms are omitted for clarity. Color code: chromium(III) ions green, oxygen red, nitrogen blue, carbon black.

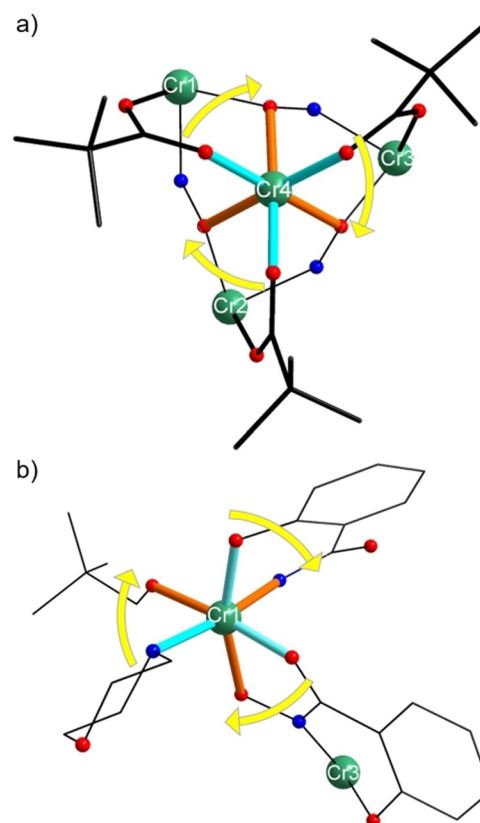


Figure 2. Schematic representation of Δ isomers of a) central chromium(III) ion Cr4 and b) ring metal ion Cr1. Color code: chromium(III) ions green, oxygen red, nitrogen blue, carbon black.

and Cr3 plane and 1.11 Å above the O3, O6, and O9 plane (see Figure S7–S8) and is additionally held by three pivalate ligands coordinated in a $\mu^2\text{-}\eta^1\text{:}\eta^2$ mode.

The $[\text{Cr}_3\text{Cr}]\text{-MC}$ was spectroscopically characterized in bulk using IR and UV/Vis spectroscopy (see SI with Figures S10 and S11). The UV/Vis spectrum of $[\text{Cr}_3\text{Cr}]\text{-MC}$ in methanol shows absorption bands at 256 nm and 356 nm which can be assigned to ligand-based $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ excitations.^[27] Two bands at higher wavelengths, 425 nm and 577 nm, can be assigned to the spin-allowed ligand field transitions from the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (F) and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F),^[28] respectively, confirming the t_{2g}^3 electron configuration.

To further elucidate the magnetic properties of the $[\text{Cr}_3\text{Cr}]\text{-MC}$, we performed variable temperature magnetic susceptibility measurements. Figure 3 shows that the $\chi_m T$ product steadily decreases when cooling, from 5.9 $\text{cm}^3\text{Kmol}^{-1}$ at 300 K to a minimum of 3.3 $\text{cm}^3\text{Kmol}^{-1}$ at about 40 K. Further lowering of the temperature leads to the $\chi_m T$ product increasing again, until a value of 4.4 $\text{cm}^3\text{Kmol}^{-1}$ is reached at 4 K. The experimental $\chi_m T$ value at 300 K is well below the theoretical value for four uncoupled $S=3/2$ spin centers calculated using the spin-only formula (7.5 $\text{cm}^3\text{Kmol}^{-1}$) indicating significant antiferromagnetic exchange interactions. The shape of the $\chi_m T$ vs. T curve further suggests the presence of competing antiferromagnetic exchange interactions.

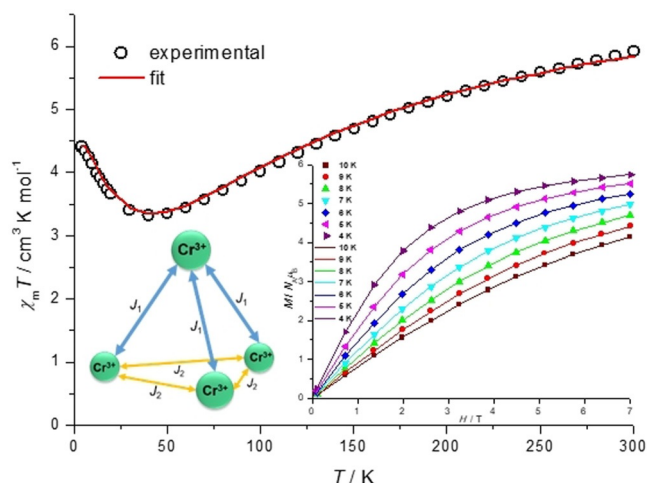


Figure 3. Temperature-dependence of magnetic susceptibility for $[\text{Cr}_3\text{Cr}]\text{-MC}$. The solid line represents the best fit of the data. Inset a) Idealized coupling scheme for metallacrown with coupling constant J_1 between guest ion (Cr_4) and ring metal ions ($\text{Cr}_1, \text{Cr}_2, \text{Cr}_3$) and coupling constant J_2 between neighboring ions (ring metal ions $\text{Cr}_1, \text{Cr}_2, \text{Cr}_3$); b) field-dependent magnetization (4–10 K). Solid lines represent the best fit of the data.

The program PHI^[29] was used to fit the susceptibility and magnetization data simultaneously using the Hamiltonian \hat{H} exchange (Equation (1)) with the coupling Scheme depicted in the inset in Figure 3. In this equation, J_1 describes the coupling constant between the guest and ring metal ions, while J_2 describes the coupling between the neighboring ring metal ions.

$$\hat{H} = -2J_1(\hat{S}_{\text{Cr}_4}\hat{S}_{\text{Cr}_1} + \hat{S}_{\text{Cr}_4}\hat{S}_{\text{Cr}_2} + \hat{S}_{\text{Cr}_4}\hat{S}_{\text{Cr}_3}) - 2J_2(\hat{S}_{\text{Cr}_1}\hat{S}_{\text{Cr}_2} + \hat{S}_{\text{Cr}_2}\hat{S}_{\text{Cr}_3} + \hat{S}_{\text{Cr}_1}\hat{S}_{\text{Cr}_3}) \quad (1)$$

The best fit was obtained for the exchange coupling constants $J_1 = -11.2 \text{ cm}^{-1}$ and $J_2 = -3.2 \text{ cm}^{-1}$ with the g factor for the chromium(III) ions fixed at $g_{\text{Cr}^{3+}} = 2.00$. The residual R was calculated to be 0.10×10^{-9} . We included a very small intermolecular antiferromagnetic interaction, implemented as mean field interaction $zJ = -0.045 \text{ cm}^{-1}$. Although this value is very low, its inclusion is necessary to obtain a satisfactory simulation of the data. Such a small intermolecular antiferromagnetic coupling is easily explained by weak dipole-dipole interactions between the chromium(III) ions of neighboring MCs ($d = 5.5 \text{ \AA}$, see Figure S1). The value of the higher antiferromagnetic interaction between the ring metal ions and the guest ion, $J_1 = -11.2 \text{ cm}^{-1}$, is in accordance with the observed average angles $\text{Cr}_{\text{ring}}\text{-O-Cr}_{\text{guest}}$ of $\approx 113^\circ$. The exchange between neighboring ring metal ions occurs exclusively via NO moieties with average torsion angles $\text{Cr}_{\text{ring}}\text{-O-N-Cr}_{\text{ring}}$ of $\approx 154^\circ$, which explains the lower value of $J_2 = -3.2 \text{ cm}^{-1}$.

Similar Cr-O-Cr bond angles as in our $[\text{Cr}_3\text{Cr}]\text{-MC}$ are reported for the above-mentioned carboxylates, $[\text{Cr}_3(\mu_3\text{-O})(\text{RCOO})_6]$ with $110\text{--}120^\circ$. For these μ_3 -oxo complexes coupling constants between -9.5 cm^{-1} and -14 cm^{-1} are reported.^[18,30,31] However, the comparison with the iron(III) metallacrown, $\text{Fe}^{\text{III}}[\mu_3\text{-O}(\text{N}(\text{sh})\text{-}3)]$,

seems more appropriate as it shows the same $\mu_2\text{-O}$ mode with an angle of 115° .^[32] The reported coupling constant is -14 cm^{-1} which matches the value obtained in our study perfectly. It is less easy to compare the antiferromagnetic exchange interaction J_2 via the $\text{Cr}^{3+}\text{-N-O-Cr}^{3+}$ coordination with examples from the literature. To the best of our knowledge, all complexes with $\text{Cr}^{3+}\text{-N-O-Cr}^{3+}$ coordination have additional bridging oxygen ligands, and the $\text{Cr}^{3+}\text{-O-Cr}^{3+}$ exchange process is considered to dominate. Moreover, the μ_3 -oxo-bridged complexes with $\text{Cr}^{3+}\text{-N-O-Cr}^{3+}$ bridges have much smaller torsion angles and are thus not comparable with the torsion angles in our $[\text{Cr}_3\text{Cr}]\text{-MC}$.^[18,19] Again, the above-mentioned iron(III) metallacrown has a comparable large torsion angle of 150° .^[32] The coupling constant within the ring for this MC was also determined as $J_2 = -3.2 \text{ cm}^{-1}$. Taking into account a dominant π -contribution for the exchange interaction via the hydroxamate group, the comparable coupling strength is easily explained by the analog electron configuration for the d^5 and d^6 metal ions regarding the t_{2g} -orbitals with π -character.

For MC complexes with competing exchange interactions, J_1 and J_2 , previous research has shown that the relative energies of the spin states are functions of the ratio between the coupling constants J_1/J_2 .^[8,33] At a ratio of J_1/J_2 close to 1, the S_T ground state with the lowest multiplicity occurs as a result of an alternating spin alignment in the cyclic scaffold. On the contrary, if J_1 coupling constants dominate, the peripheral spins align antiparallel to the central spin. In our study, we extracted a J_1/J_2 ratio of 3.5 and showed that the antiferromagnetic coupling J_1 of the guest ion with the ring metal ions is slightly dominant, thus forcing the coordination cluster into a high spin ground state of $S_T = 3$.

To confirm this ground state, we performed field-dependent magnetization measurements between 4 K and 10 K in an applied field of 0 to 7 T (see insert Figure 3 and S15). Although the magnetization increases rapidly, it does not reach saturation. However, extrapolation of the saturation value in higher fields is consistent with six unpaired electrons, indicating a spin ground state of $S_T = 3$. (For the simulation of the Zeeman splitting see Figures S13 and S14)

In conclusion, we synthesized the long-sought missing chromium metallacrown $\{\text{Cr}^{\text{III}}(\mu_2\text{-piv})_3[\mu_3\text{-O}(\text{N}(\text{sh})\text{-}3)](\text{morph})_3\}\cdot\text{MeOH}$, which was predicted over 30 years ago.^[8] The structure corresponds to predictions made based on the iron(III) metallacrown. The magnetic analysis revealed two competing antiferromagnetic exchange interactions, resulting in a spin ground state of $S_T = 3$. This first successful chromium(III) MC synthesis paves the way for new kinetically and thermodynamically stable MCs which can be used in multiple applications. We will continue this line of research with the aim of implementing other ions in chromium metallacrown cavities.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: 9-MC-3 · chromium · kinetic stability · metallacrown · structural integrity

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