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Constructing Cr^{III}-centered heterometallic complexes: [Ni$^{II}_6$Cr^{III}] and [Co$^{II}_6$Cr^{III}] wheels

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The solvothermal reaction between Cr(acac)$_3$, MCl$_2$·6H$_2$O (M= Ni, Co) and 2-hydroxy-4-methyl-6-phenyl-pyridine-3-amidoxime (H$_2$L), under basic conditions, led to the synthesis of the heterometallic heptanuclear clusters [M$^{II}_6$Cr(HL$_{zw}$)$_6$(HL)$_6$]·3Cl (M= Ni, 1; Co, 2), with the nickel analogue displaying an S= 9/2 spin ground-state.

During the last few years the field of molecular magnetism has witnessed an exponential development and growth; single-molecule and/or single-ion magnets with extremely high energy barriers (>1000 K) for the re-orientation of the magnetization have been reported,[1] and species can now remain magnetized upon the removal of an external magnetic field at temperatures as high as T_b= 60 K,[2] a feature long-awaited and anticipated since the early stages of single-molecule magnetism.[3] This is not only the outcome of "serendipitous self-assembly" which governs the formation of polynuclear species,[4] but the result of numerous synthetic efforts, computational studies and theoretical treatment of spectroscopic data, towards the deeper understanding of the underlying principles of molecular magnetism. As a result, lanthanides now are considered as major players in molecular magnetism,[5] replacing traditional metal centres such as manganese, iron, cobalt and nickel which dominated the early era of single-molecule magnetism.[6] Yet, 3d transition metals offer two main advantages over the 4f centres: i) they are important in the construction of large clusters due to their well-defined geometries, and ii) they offer good candidates for the understanding of the magnetic exchange interactions between neighboring metal centres,

since there are various theoretical models that can be safely applied to such systems.

With the above in mind, we engaged in a project to construct heterometallic Ni^{II}/Cr^{III} clusters upon employment of the amidoxime ligand 2-hydroxy-4-methyl-6-phenyl-pyridine-3-amidoxime, H$_2$L (Scheme 1), and herein we present the synthesis of a heptametallic heteronuclear [Ni$^{II}_6$Cr^{III}] complex, as well as its Co^{II} analogue.

Cr(acac)$_3$ (0.75 mmol, 262 mg), NiCl$_2$·6H$_2$O (0.6 mmol, 143 mg), H$_2$L (1 mmol, 243 mg) and NEt$_3$ (1 mmol) were dissolved in MeOH (15 ml), and the reaction mixture was transferred to a Teflon-lined autoclave and heated at 120 °C for 12 hours. The autoclave was allowed to cool slowly to room temperature, and the resulting brown solution was layered with Et$_2$O to form dark-brown crystals of [Ni$^{II}_6$Cr(HL$_{zw}$)$_6$(HL)$_6$]Cl$_3$·15.5MeOH·3.25H$_2$O (**1**·15.5MeOH·3.25H$_2$O) in ~ 35% yield (HL$_{zw}$: the *zwitterionic* form of the ligand). In an analogous manner, upon using CoCl$_2$·6H$_2$O instead of NiCl$_2$·6H$_2$O, we were able to isolate complex [Co$^{II}_6$Cr(HL$_{zw}$)$_6$(HL)$_6$]Cl$_3$·Et$_2$O·17.5MeOH·H$_2$O (**2**·Et$_2$O·17.5MeOH·H$_2$O) in ~ 30% yield.
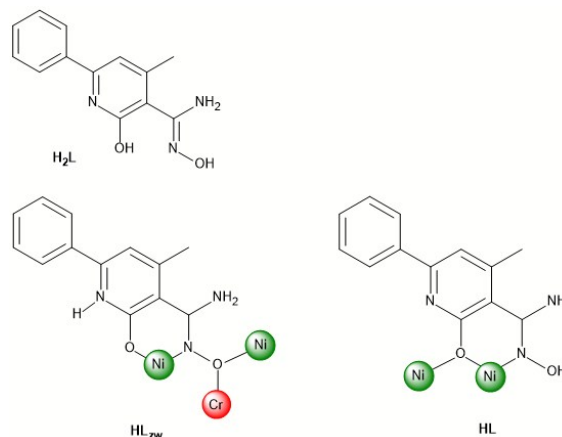
Scheme 1. The ligand employed in this work and its coordination modes in **1**.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Complexes **1** and **2** (Fig. S1) are isostructural, so for the sake of brevity we will only describe the crystal structure of complex **1.** Complex **1** (Fig. 1, top) crystallizes in the monoclinic space group $P2_1/n$. Its core (Fig. 1) consists of a planar Cr^{III}-centered Ni_6 wheel, assembled by i) six μ_3 $(-N-O-)_{oximate}$ groups belonging to six *zwitterionic* η^2: η^1: η^1: μ_3 ligands, HL_{zw}^-, and ii) six μ alkoxide groups from six mono-deprotonated η^2: η^1: μ ligands, HL^-. The six Ni^{II} ions describe an almost planar regular hexagon (with all Ni-Ni-Ni angles ≈ 120°), with the trivalent chromium ion located at its centre. The Ni-Ni distances are ≈3.5 Å, while the Ni-Cr distances are ≈3.4 Å. All Ni^{II} ions are six-coordinate with an N_2O_4 coordination environment, adopting octahedral geometry, while the "harder" Cr^{III} ion has an O_6 octahedral sphere. In the solid state, molecules of **1** along with the solvate methanol and aqua molecules and chloride anions are H-bonded creating a complex 3D H-bonded framework (Fig. S2).
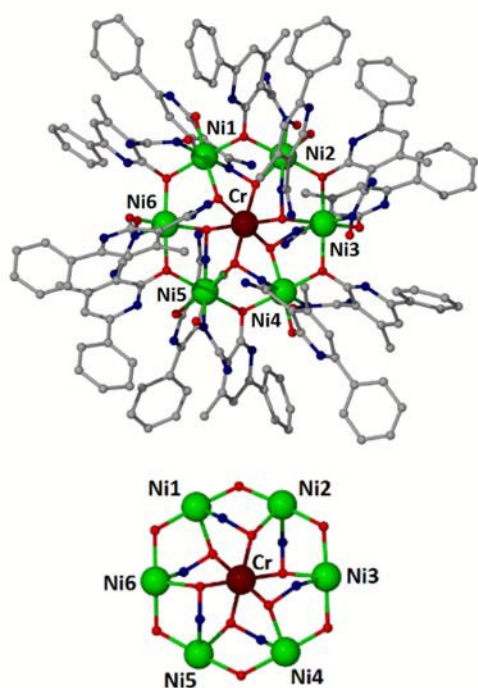

Figure 1. The molecular structure of **1** (top), and its core (bottom). Colour code: Cr(III) = brown; Ni(II) = green; O = red; N = blue; C = grey.

Variable temperature dc magnetic susceptibility measurements were collected for both **1** and **2** in the temperature range 2.0 – 300 K, under an applied magnetic field of 0.1 T, and are plotted as $\chi_M T$ versus T in Figure 2. For **1**, the room temperature $\chi_M T$ value of 7.91 cm³ K mol⁻¹ is slightly lower than the expected value of 8.49 cm³ K mol⁻¹ for six non-interacting Ni^{II} (g = 2.10) and one Cr^{III} (g = 2.00) ions. Upon cooling the value of $\chi_M T$ decreases slowly to 7.10 cm³ K mol⁻¹ at ~ 130 K , below which it increases rapidly to the maximum value of 14.11 cm³ K mol⁻¹ at 10 K, before reaching the final value of 13.38 cm³ K mol⁻¹ at 2 K. This behavior indicates the presence of competing ferro- and antiferro-magnetic interactions, with the lowest temperature $\chi_M T$ value suggesting an $S ≈ 9/2$ ground state, while the low-T

drop may be attributed to either Zeeman effects, zero-field splitting or intermolecular interactions. We were able to successfully fit the magnetic susceptibility data using the *2-J*
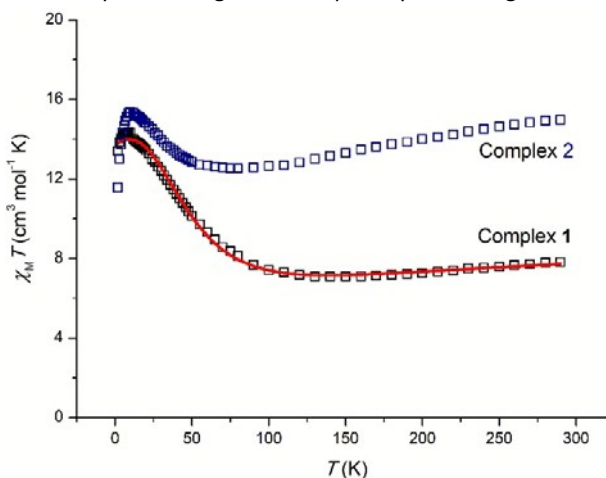

Figure 2. $\chi_M T$ *vs.* T plot for complexes **1** and **2** under an applied *dc* field of 0.1 T. The solid line represents fit of the data in the 2 – 300 K (see text for details).

model shown in Figure 3 and the Hamiltonian equation (1), which assumes the following exchanges interactions: i) one exchange, J_1, between neighboring Ni^{II} ions, mediated by one monoatomic alkoxide group from a mono-deprotonated η^2: η^1: μ ligand (with Ni- O $_R$-Ni angles in the narrow 112-114° range) and one $-N-O_{-oximate}$ group belonging to a η^2: η^1: η^1: μ_3 HL_{zw}^- ligand, with Ni-O-N-Ni torsion angle of ~58°, and ii) one exchange, J_2, between $Ni^{II}-Cr^{III}$ centres mediated by one monoatomic oximate group (*via* the oximate O atom with Ni- O -Cr angle ~ 111°) and one $-N-O_{-oximate}$ group belonging to a η^2: η^1: η^1: μ_3 HL_{zw}^- ligand, with Ni-O-N-Cr torsion angle of ~64°. Using the program PHI,[7] and employing the Hamiltonian in eqn. (1)

$$\hat{H} = -2J_1\,(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4 + \hat{S}_4 \cdot \hat{S}_5 + \hat{S}_5 \cdot \hat{S}_6 + \hat{S}_1 \cdot \hat{S}_6) - 2J_2\,(\hat{S}_1 \cdot \hat{S}_7 + \hat{S}_2 \cdot \hat{S}_7 + \hat{S}_3 \cdot \hat{S}_7 + \hat{S}_4 \cdot \hat{S}_7 + \hat{S}_5 \cdot \hat{S}_7 + \hat{S}_6 \cdot \hat{S}_7)\ (1)$$

afforded the parameters J_1 = 5.1 cm⁻¹ and J_2 = -11.5 cm⁻¹, with g_{Ni} = 2.10 and g_{Cr} = 2.00. The ground state of **1** was found to be S = 9/2 with the first excited state (S = 7/2) located ~ 44 cm⁻¹ above. The ferromagnetic nature of J_1 should mainly be attributed to the long $-N_{ox}-O_{ox}-$ bonding distance of ~ 1.4 Å, which has been found to propagate ferromagnetic interactions in nickel oximate complexes,[8] while in addition such ferromagnetic interaction has been reported previously in nickel complexes with $-N_{ox}-O_{ox}-$ and alkoxide doubly bridged Ni pairs, as in **1**.[9] The antiferromagnetic nature of the $Ni^{...}Cr$ exchange J_2 is not so surprising.[10] Ferromagnetic exchange between Cr(III) and Ni(II) is expected if both metal ion sites are in O_h symmetry leading to strictly orthogonal magnetic orbitals.[11] In **1** the site symmetry is lower and d orbital mixing could lead to antiferromagnetic contributions to J_2. Furthermore in $\{Ni(-N_{ox}-O_{ox})_3-Cr\}$ dimeric species

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antiferromagnetic exchange has been observed (-9.2 cm^{-1} and -5.1 cm^{-1}).[12]

For the cobalt analogue, complex **2**, the room temperature $\chi_M T$ value of 14.97 cm^3 K mol^{-1} is below that expected for six non-interacting octahedral Co^{II} ($g > 2.3$) and one Cr^{III} ($g = 2.00$) ions. Upon cooling, the value of $\chi_M T$ decreases steadily to 12.60 cm^3 K mol^{-1} at ~ 65 K, while upon further lowering the temperature it increases at the maximum value of 15.36 cm^3 K mol^{-1} at ~ 10 K, before reaching the final value of 11.56 cm^3 K mol^{-1} at 2 K. Given the presence of six octahedral Co^{II} ions, each with a $^4T_{1g}$ ground term and first order spin-orbit coupling,[13] it is difficult to draw any solid conclusions regarding the magnetic behaviour of **2**. Yet, the high temperature $\chi_M T$ decrease may be attributed to the zero-field splitting of the Co^{II} ions, while the subsequent increase may be attributed to the competing F/AF interactions, as found in complex **1**.
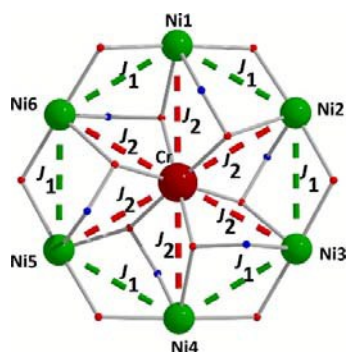

Figure 3. *J*-interaction scheme employed for fitting the magnetic susceptibility measurements for complex **1** (see text for details).

In order to verify the above mentioned ground-state for complex **1**, magnetization data were collected in the ranges 0.04 − 5 T and 2 − 6 K and these are plotted as reduced magnetization ($M/N\mu_B$) *vs. H* in Figure 4. The data were fit by a matrix diagonalization method to a model that assumes only the ground state is populated, includes axial zero-field splitting ($D\hat{S}_z^2$) and the Zeeman interaction, and carries out a full powder average. The corresponding Hamiltonian is given by equation (2), where D is the axial anisotropy, μ_B is the Bohr magneton, μ_0 is the vacuum permeability, $\hat{S}_z$ is the easy-axis spin operator, and H is the applied field. The best fit gave $S = 9/2$, $g = 2.08$ and $D = -0.33$ cm^{-1}.

$$\hat{H} = D\hat{S}_z^2 + g\mu_B\mu_0\hat{S}\cdot H \qquad (2)$$

Given the relatively high spin ground-state of complex **1** ($S = 9/2$) and its negative and large D value (-0.33cm^{-1}), we performed *ac* magnetic susceptibility studies in order to investigate single molecule magnetism behaviour for the complex. However, no out-of-phase, χ_M'', signals were observed for **1**, thus ruling out the possibility of slow relaxation of the magnetisation.
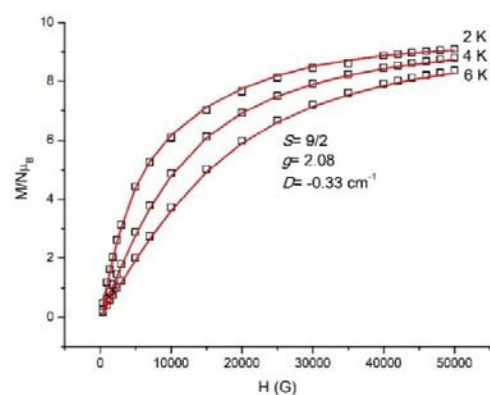

Figure 4. Plot of reduced magnetization ($M/N\mu_B$) *vs. H* for **1**, in fields 0.04 − 5 T and temperatures 2-6 K.

Conclusions

In conclusion, in this work we report the synthesis and characterisation of two novel heptanuclear [M$^{II}_6$Cr^{III}] complexes (M=Ni, **1**; Co, **2**), upon employment of a new amidoxime ligand. Both clusters are isostructural, adopting a M$^{II}_6$ wheel topology, encapsulating a Cr^{III} ion at its centre.

To the best of our knowledge, and following a thorough CCDC search, these two clusters represent the first examples of Ni^{II} (or Co^{II}) rings encapsulating a central Cr^{III} ion; a surprising feature given the extended research on heterometallic molecular Cr/Ni(or Co) rings reported so far.[14] Synthetic efforts are currently underway in order to isolate other analogues of these wheels, upon either replacing the central "hard" chromium ion with other trivalent centres, or upon making mixed-metal peripheral rings.

Conflicts of interest

There are no conflicts to declare.

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Constructing Cr^III-centered heterometallic complexes: [Ni^II_6Cr^III] and [Co^II_6Cr^III] wheels

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The syntheses, structures and magnetic properties of two Cr^III-centered wheels, [M^II_6Cr^III] (M= Ni, Co), are reported.