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· Communication

Self-Assembly of a Nonanuclear Nickel(II) Complex and Its Magnetic Properties

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A nonanuclear nickel(II) complex [Ni$_9$(PyA)$_{10}$(μ_3-OH)$_2$(μ_2-OH)$_2$(μ_2-OH)$_2$(H$_2$O)$_6$](ClO$_4$)$_4$·12H$_2$O, containing pyridine-2-aldoximato monoanion, PyA, has been structurally and magnetochemically characterized. The nickel(II) ions, linked together via several bi- or trifurcated oximato, hydroxo, and water bridges, are antiferromagnetically coupled with the coupling constants $J_1 = -26.5$ cm^{-1} and $J_2 = -7.0$ cm^{-1}, resulting in a ground state of $S_t = 1$.

Complexes containing two or more metal ions are of increasing interest because of their relevance to biological systems (as evidenced by the many multinuclear complexes in biology)[1] and to molecular magnetism.[2] Polynuclear systems are ideal candidates for the synthesis of single-molecule magnets (SMMs).[3] The prerequisites for molecules to show SMM behavior are the presence of a high-spin ground state and a significant negative zero-field-splitting parameter *D*. So, the interest in polynuclear complexes[4] of 3d transition metals has been augmented by the search for new magnetic clusters. Despite the interest in the properties of such systems, synthetic methods have yet to reach the level of efficiency attained with mononuclear complexes.

The oxime ligands[5] can connect two metal ions owing to their versatility in coordination ability. That the oximate as bridging ligands can efficiently transmit exchange coupling[6]

has also been well documented. Among the exchange-coupled oximate-bridged nickel(II) complexes structurally characterized during the last 30 years, there are only a few complexes that have been subjected to variable-temperature magnetic susceptibility measurements.[7] As a result of this scarcity of available data, no magnetostructural correlation has yet been obtained; hence, more oximate-bridged paramagnetic complexes of nickel(II) are warranted. Moreover, nickel(II) is known to have a large single-ion zero-field splitting and often gives rise to ferromagnetic coupling;[8] thus, polynuclear nickel(II) complexes are potential candidates for SMMs.[9]

The complexation between nickel(II) and pyridine-2-aldoxime, HPyA, in an aqueous solution was studied by Orama et al.;[10] the structure in the solid state was found to consist of two monomeric neutral tris complex [Ni(PyA)$_2$(PyAH)]^0 units held together by two hydrogen bondings, O··H···O. On the contrary, for copper(II) the presence of the trinuclear species [Cu$_3$(PyA)$_3$(OH)]$^{2+}$ containing the central core Cu$_3$OH in both an aqueous solution and the solid state has been documented.[11] We herein report a nonanuclear nickel(II) complex with a *syn*-pyridine-2-aldoxime ligand, [Ni$_9$(PyA)$_{10}$(μ_3-OH)$_2$(μ_2-OH)$_2$(μ_2-OH$_2$)$_2$(OH$_2$)$_6$](ClO$_4$)$_4$·

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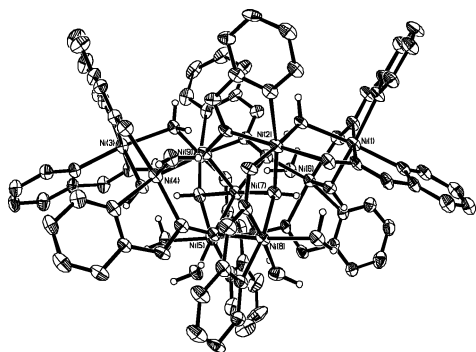
Figure 1. ORTEP view of the Ni^{II}_9 complex.

$12H_2O$ (**1**), underlining the versatility of this oxime ligand to adopt a variety of coordination modes yielding a nonanuclear nickel(II) complex. There are very few nonanuclear nickel(II) complexes known that have been characterized magnetically.[12]

The nonanuclear complex **1** was isolated as a light-orange microcrystalline solid from an aqueous solution of pH 8.0, adjusted with dilute NaOH, containing $NiCl_2·6H_2O$ and HPyA in a 1:1 molar ratio, to which $NaClO_4$ was added as the counteranion. One of the single crystals[13] obtained by slow evaporation of a methanol−water (2:1) solution of **1** was used to determine the molecular structure by X-ray crystallography at 100 K (Figure 1). The lattice consists of a discrete nonanuclear tetracation, 4 perchlorate anions, and 12 water molecules of crystallization. There are two types of oximic groups: (i) two-atom N−O bridging groups, N2−O1, N12−O11, N32−O31, N42−O41, N52−O51, and N82−O81, and (ii) μ_2-O bridging oximates, O21, O61, O71, and O91. The nonanuclear complex can be described as two $[Ni^{II}_4(PyA)_5(\mu_3\text{-OH})(\mu_2\text{-OH})(\mu\text{-OH}_2)(H_2O)_3]^+$ moieties connected to a centrally placed Ni(II) ion, Ni7, through four μ_3-oximate oxygens, O21, O61, O71, and O91, and two trans-disposed μ_3-OH groups, O153 and O156, thus yielding an octahedral Ni7−O_6 core. As shown in Figure 2, a schematic view of the Ni_9 core structure, there are two identical NiN_4O_2 environments for Ni1 and Ni3 with two pyridine nitrogens, two oxime nitrogens, one μ_2-OH, and one μ_2-OH$_2$ bridging groups. All of the oxime groups are deprotonated, and the nickel atoms are linked together via bi- or trifurcated oximato, hydroxo, and water bridges. There are three types of NiN_2O_4 cores in which the pairs Ni2−Ni9, Ni4−Ni6, and Ni5−Ni8 possess the same types of donor atoms. The ligand atoms around Ni2 and Ni9 are one pyridine nitrogen, one oximic nitrogen, one μ_3-OH, two oximate oxygens, and one μ_2-OH$_2$ bridging oxygen. The coordination environment around Ni4 and Ni6 differs from that for the Ni2−Ni9 pair in that there are, instead of two, only one μ_2-bridging oxygen oximate, one μ_2-OH (instead
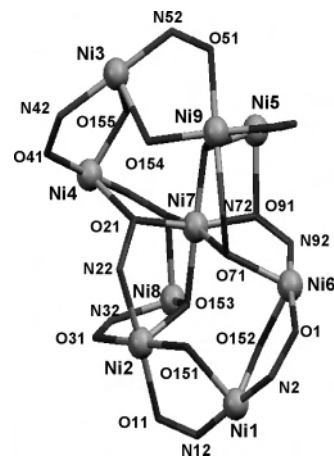

Figure 2. Metallic core in the Ni^{II}_9 complex.

of μ_3-OH), and a coordinated water. Ni5 and Ni8 are also in a N_2O_4 octahedral environment, with one pyridine nitrogen, one oximic nitrogen, one μ_2-bridging oximate oxygen, one μ_3-OH, and two terminally coordinated water groups. The metal core might be described as a centered hexagonal bipyramid of nickels (Figure 2). A similar nonanickel(II) has been described in the literature.[14]

There are at least eight strong hydrogen bondings prevailing between the oximate, hydroxo, and water oxygens (Supporting Information). The eight hydrogen atoms bonded to the bridging oxygens are observed. The O···H···O bond lengths lie in a small range of 2.63−2.76 Å and presumably are responsible for building up the supramolecular structure in **1**. The average C=N, −N−O$_{ox}$−, and −N−μ_2-O$_\alpha$ bond distances are 1.280, 1.347, and 1.378 Å, respectively, which are identical with those in other comparable structures.[15] The Ni−O$_{ox}$ distances lie in the range of 2.005−2.174 Å and are in accordance with the expectation that Ni−μ_2-O$_{ox}$ bond lengths are significantly longer than the Ni−O$_{ox}$ distances. The Ni−N bond distances are consistent with normal covalent bonds for high-spin Ni(II) d^8 ions with oximate ligands. The μ_3-O153H acts as a bridge between Ni2, Ni7, and Ni8. Similarly, O156H is a μ_3-bridging ligand for Ni5, Ni7, and Ni9. The hydroxide ions, O152H and O155H, act as μ_2-bridging ligands between Ni1, Ni6 and Ni3, Ni4, respectively. In the cluster there are two different sets of Ni−O−Ni bond angles lying in the ranges of 93.7−102.2° and 108.4−114.6°.

The magnetic susceptibility data for polycrystalline samples of **1** were collected in the temperature range of 2−290 K in an applied magnetic field of 1 T and are displayed as squares in Figure 3 as a plot of the magnetic moment (μ_{eff}) vs temperature (T). The effective magnetic moment of $\mu_{eff} = 8.20\ \mu_B$ ($\chi_M T = 8.40\ cm^3\ mol^{-1}\ K$) for **1** at 290 K is smaller than the spin-only value expected for nine isolated Ni(II) ions of $\mu_{eff} = 8.49\ \mu_B$ with $g_{Ni} = 2.0$, indicating an overall antiferromagnetic spin coupling between the Ni(II) centers. Accordingly, the magnetic moment decreases monotonically

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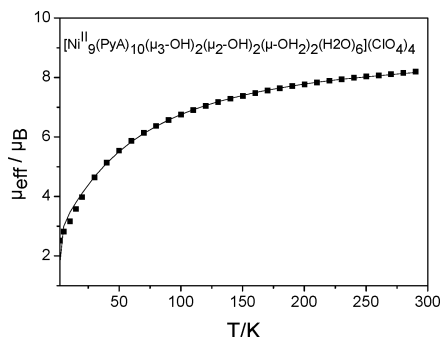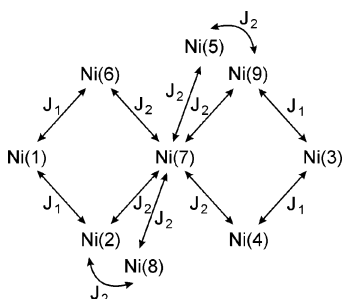
Figure 3. Plot of the effective magnetic moment as a function of temperature. The solid line represents the best least-squares fit parameters given in the text.

Chart 1

with decreasing temperature, reaching a value of $\mu_{eff} = 2.51$ μ_B ($\chi_M T = 0.79$ cm^3 mol^{-1} K) at 2 K.

A close examination of the structure indicates that there are five different types of bridging groups for transmission of exchange coupling between the Ni(II) centers with $S_{Ni} = 1.0$: (i) diatomic $-NO-$, (ii) μ_3-oximate $-N-O$, (iii) μ_2-OH, (iv) μ_3-OH, and (v) μ_2-OH$_2$. To avoid overparametrization, we have considered a model, shown as the coupling scheme in Chart 1, with two exchange-coupling constants J_1 and J_2, where J_1 represents the interactions through $-N-O-$ and μ_2-OH groups, whereas J_2 represents the paths involving μ_3-oximate, $-N-O$ and μ_3-OH groups. We have neglected the exchange path involving μ_2-OH$_2$ because the exchange coupling for the Ni(II) centers through μ_2-OH$_2$ is reported to be negligibly small.[16] We have used the simplest model, viz., a two-J model, in order to make it possible to analyze the magnetic data. In other words, with a single coupling constant that takes into account all exchange pathways to be equal, it is not possible to simulate the experimental data.

Such a complicated magnetic structure represents an interesting challenge for fitting and interpreting the susceptibility data. The total spin degeneracy for nonanuclear Ni(II) is 3^9, i.e., 19 683, which leads to a matrix 19 683 × 19 683 to be diagonalized for simulation of the experimental data. So, it is apparent that procedures are required that employ symmetry in order to reduce the dimension of the matrices. We
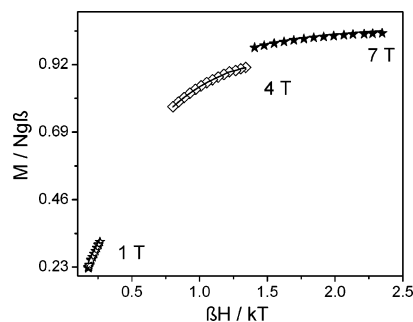
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Figure 4. Plot of VTVH measurements. The solid line represents the best least-squares fit parameters given in the text.

have reduced the matrix to 243 × 243 (=3^5) by considering five nickel centers because the structural data indicate that two tetranickel units are connected with the central Ni7. The exchange-coupling model shown in Chart 1 was considered for simulation of the experimental magnetic data using the irreducible tensor operator approach[17] with the Heisenberg Hamiltonian in the form of $H = -2J\hat{S}_i\hat{S}_j$. The best-fit parameters obtained from the simulation shown as the solid line in Figure 3 are $J_1 = -26.5$ cm^{-1}, $J_2 = -7.0$ cm^{-1}, with $g = 2.15$. That the J_1 interaction through the diatomic NO bridging is stronger than the J_2 interaction mediated through the μ_3-oximate oxygen is in accordance with the corresponding literature values.[15] All so-far-reported oximate-bridged nickel(II) complexes[6] exhibit moderate to weak antiferromagnetic interactions lying between $J = -7$ and -40 cm^{-1}. That complex **1** with nine nickel(II) centers, $S_{Ni} = 1.0$, possesses an $S_t = 1.0$ ground state has also been confirmed by the variable-temperature (2−4 K) and variable-field (1, 4, and 7 T) magnetization (VTVH) measurements (Figure 4). From the best fit with a fixed $S = 1.0$, we have evaluated the zero-field-splitting parameter D to be $D_{S=1} = 2.7$ cm^{-1} with $g = 2.14$. We want to stress that all of our attempts to fit the VTVH measurements with a negative D value failed.

To conclude, we have utilized the polymetallic bridging ability of an oxime, HPyA, to self-assembly a nonanuclear Ni(II) complex that has been magnetochemically characterized to possess an $S_t = 1.0$ ground state with $D = +2.7$ cm^{-1}.

Supporting Information Available: Details of the X-ray structural data, a perspective view of the hydrogen bonding in a Ni$^{II}_9$ cluster, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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