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Acetate/Di-2-pyridyl Ketone Oximate "Blend" as a Source of High-Nuclearity Nickel(II) Clusters: Dependence of the Nuclearity on the Nature of the Inorganic Anion Present

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The use of di-2-pyridyl ketone oxime [$(py)_2CNOH$] in reactions with $Ni(O_2CMe)_2{\cdot}4H_2O$, in the presence or absence of extra inorganic anions (N_3^- and SCN^-) has led to Ni_4, Ni_5, and Ni_7 clusters; the magnetic study of the heptanuclear nickel(II) complex reveals an $S = 3$ ground state.

Synthetic access to high-nuclearity 3d metal clusters has allowed the experimental observation of exciting phenomena in the field of molecular magnetism, such as "single molecule magnetism",[1] and the study of synthetic models of the active sites in metallobiomolecules.[2] However, the factors that influence the synthesis of high-nuclearity clusters are still not well understood; thus, there is a continuing need for new synthetic procedures to such species. There are two main trends in the field: the "designed synthesis"[3] and the "serendipitous assembly".[4] The latter approach lacks control over the product, but it has proven to be extremely successful in the synthesis of clusters with interesting properties;[5] it uses flexible organic ligands that impose little or no geometry. One such ligand is di-2-pyridyl ketone oxime [IUPAC name: dipyridin-2-yl-methanone oxime, $(py)_2CNOH$], whose anion is a versatile ligand for a variety of research objectives.[6]

We have been exploring "ligand blend" reactions involving $(py)_2CNO^-$ and carboxylates as a means to high-nuclearity species. Our results with Cr,[7] Mn,[8] Fe,[9] Co,[10] and Cu[11] have been very encouraging. We have thus decided to extend the exploration of the general $(py)_2CNO^-/RCO_2^-$ "blend" in Ni chemistry, and we can now report that the $Ni^{II}/(py)_2CNO^-/MeCO_2^-$ reaction system has provided access to tetra-, penta-, and heptanuclear clusters.

The reaction between $Ni(O_2CMe)_2{\cdot}4H_2O$ and $(py)_2CNOH$ in a 1:1 molar ratio in Me_2CO/H_2O (5:1, v/v) gave a dark-red solution from which, upon slow evaporation at room temperature, dark-red crystals of the neutral complex $[Ni_5(O_2CMe)_7\{(py)_2CNO\}_3(H_2O)]{\cdot}0.5Me_2CO{\cdot}3.2H_2O$ (**1**$\cdot 0.5Me_2CO{\cdot}3.2H_2O$) were subsequently isolated in 60% overall yield. The molecular structure[12] of complex **1** (Figure 1) consists of five Ni^{II} atoms in a closed, cagelike arrangement. The

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(12) Crystal structure data for **1**$\cdot 0.5Me_2CO{\cdot}3.2H_2O$: $C_{48.5}H_{56.4}Ni_5N_9O_{21.7}$, $M_w = 1406.10$, monoclinic, space group $P2_1/n$ with $a = 16.8789(15)$ Å, $b = 25.140(2)$ Å, $c = 18.2298(16)$ Å, $\beta = 113.630(3)°$, $V = 7086.8(10)$ Å^3, $T = 298$ K, $Z = 4$, R1 $[I > 2\sigma(I)] = 0.0764$, wR2 $= 0.2058$ (F^2, all data). Crystal structure data for **2**$\cdot 2.2MeOH{\cdot}1.7H_2O$: $C_{51.2}H_{51.2}Ni_4N_{13}O_{12.9}S$, $M_w = 1321.90$, triclinic, space group $P\bar{1}$ with $a = 16.390(13)$ Å, $b = 15.295(11)$ Å, $c = 14.013(10)$ Å, $\alpha = 73.92(2)°$, $\beta = 69.26(3)°$, $\gamma = 66.57(3)°$, $V = 2976(4)$ Å^3, $T = 298$ K, $Z = 2$, R1 $[I > 2\sigma(I)] = 0.0604$, wR2 $= 0.1752$ (F^2, all data). Crystal structure data for **3**$\cdot 2MeCN{\cdot}12.2H_2O$: $C_{82}H_{100.4}Ni_7N_{26}O_{32.2}$, $M_w = 2376.32$, monoclinic, space group $P2/a$ with $a = 21.475(9)$ Å, $b = 21.955(9)$ Å, $c = 11.352(5)$ Å, $\beta = 96.393(12)°$, $V = 5319(4)$ Å^3, $T = 298$ K, $Z = 2$, R1 $[I > 2\sigma(I)] = 0.0453$, wR2 $= 0.1307$ (F^2, all data).

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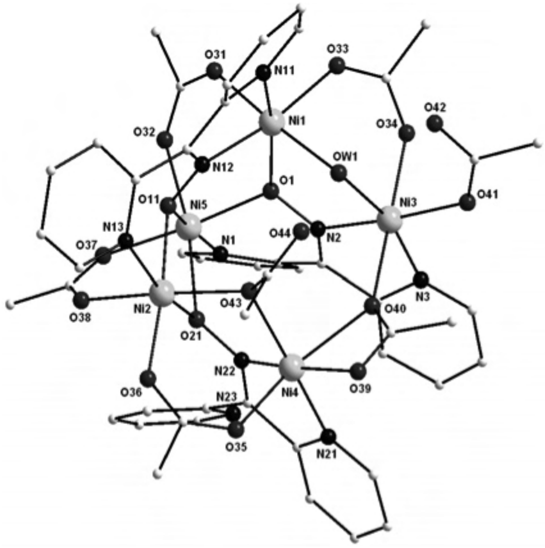
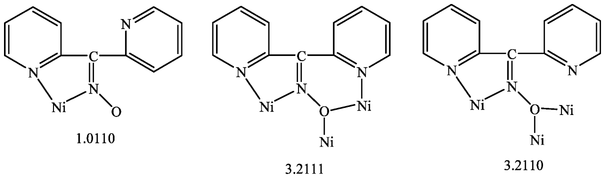


Figure 1. Molecular structure of complex **1** with selected atom labeling.

Chart 1. Crystallographically Established Coordination Modes of $(py)_2CNO^-$ in Complexes **1**−**3** and the Harris Notation That Describes These Modes



metal ions are held together through acetate, oximate, and aquo ligands. All Ni^{II} atoms are distorted octahedral. Two $(py)_2CNO^-$ ions function as 3.2111 ligands (Harris notation;[13] Chart 1), forming five-membered (NCCNNi) and six-membered (NCCNONi) chelating rings around two Ni^{II} atoms with the deprotonated oximato O atom bound to an extra Ni^{II} atom (Ni1 and Ni5). The third $(py)_2CNO^-$ group behaves as a 3.2110 ligand, with the deprotonated oximato O atom bridging two Ni^{II} atoms (Ni2 and Ni5), leaving the second 2-pyridyl N atom (N23) unbound. The seven $MeCO_2^-$ groups adopt four different coordination modes. Four of them are bound through the familiar 2.11 mode (those containing O31/O32, O33/O34, O35/O36, and O37/O38), and the remaining three are arranged in the relatively rare 2.21 (O39/O40), 2.20 (O43), and 1.10 (O41) modes. Ni1 and Ni3 atoms are further bridged by an O atom (OW1) that belongs to the aquo ligand, which is hydrogen-bonded to the uncoordinated acetate O atoms O42 and O44.

The addition of SCN^- ions to the 1:1 $Ni(O_2CMe)_2{\cdot}4H_2O$/$(py)_2CNOH$ reaction mixture in MeOH gave the acetate-poor, cationic cluster $[Ni_4(O_2CMe)_2\{(py)_2CNO\}_4](SCN)(OH){\cdot}2.2MeOH{\cdot}1.7H_2O$ (**2**$\cdot 2.2MeOH{\cdot}1.7H_2O$)[12] (Figure 2). The core consists of a tetrahedron of octahedral Ni^{II} atoms linked together by four 3.2111 (Chart 1) $(py)_2CNO^-$ ligands and two 2.11 $MeCO_2^-$ groups to form a distorted $[Ni_4(NO)_4]^{4+}$ "cube" comprising single (O) and double (N−O) atom edges. Peripheral ligation is provided by the eight 2-pyridyl N and the four acetate O atoms.

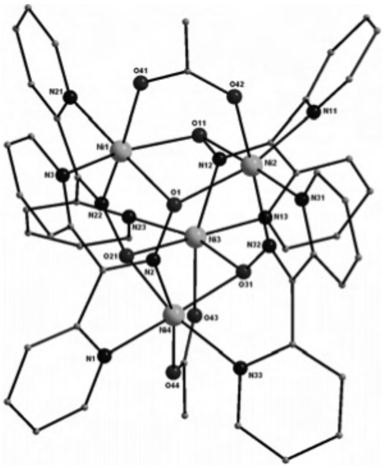


Figure 2. Partially labeled Pov−Ray representation of the cation of **2**.

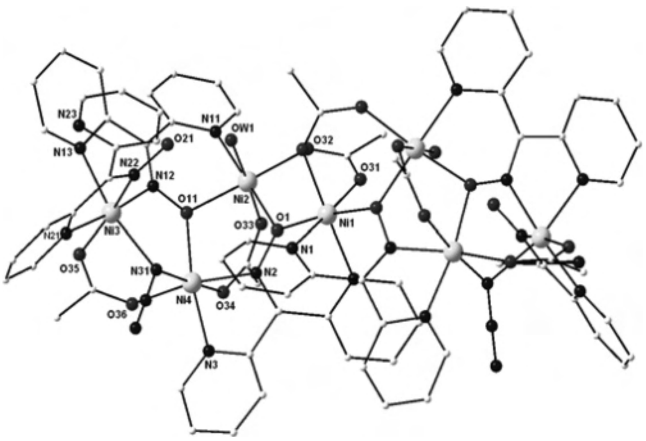


Figure 3. ORTEP representation of complex **3**.

Incorporation of N_3^- ions into the reaction system that led to **1**, but using $MeCN/H_2O$ (5:1, v/v) instead of Me_2CO/H_2O (5:1, v/v) for a better quality of single crystals, gave a dark-red solution. Layering of this solution with Et_2O and slow mixing by diffusion led to the formation of dark-red crystals of $[Ni_7(N_3)_2(O_2CMe)_6\{(py)_2CNO\}_6(H_2O)_2]{\cdot}2MeCN{\cdot}12.2H_2O$ (**3**$\cdot 2MeCN{\cdot}12.2H_2O$) in 55% yield.

The structure[12] consists of an unusual assembly of seven distorted octahedral Ni^{II} centers lying on crystallographic 2-fold axis, which passes through Ni1 (Figure 3). The molecule is held together by two end-on azido ligands (2.100), four 3.2111 $(py)_2CNO^-$ ions, and six 2.11 $MeCO_2^-$ groups. Peripheral ligation is provided by two 1.0110 $(py)_2CNO^-$ ligands (Chart 1), which bind as bidentate chelates to Ni3 (and to its symmetry-related partner), and two terminal aqua ligands, which complete the coordination sphere of Ni2 (and its symmetry-related metal ion). Without considering the bridging acetates as part of the core, the latter appears to be $[Ni_7(\eta^1{:}\mu\text{-}N_3)_2(\mu_3\text{-}ON)_4]^{8+}$. The molecule can be conveniently described as consisting of two $[Ni_3(\mu\text{-}N_3)(\mu\text{-}O_2CMe)_2(\eta^1\text{-}O_2CMe)\{\mu_3\text{-}(py)_2CNO\}\{\mu\text{-}(py)_2CNO\}\{\eta^2\text{-}(py)_2CNO\}]^-$ subunits, each linked to the central Ni1 ion through one acetate O atom (O31 and O31′), one oximate O atom (O1 and O1′), and one 2-pyridyl N atom (N1′ and N1); as a result of this connection, the terminal acetates of the hypothetical subunits become bidentate bridging, while the

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oximate O atoms (O1 and O1′) become bridging and the uncoordinated 2-pyridyl N atoms (N1′ and N1) bind to Ni1, giving an overall μ_3 character in the corresponding $(py)_2CNO^-$ ligands. Complex **3** joins a small family of structurally characterized heptanuclear nickel(II) clusters with O and/or N ligation.[14]

The $\chi_M T$ value for **1** is 4.34 cm^3 K mol^{-1} at room temperature. As the temperature is lowered, $\chi_M T$ experiences a gradual decrease, reaching a value of 0.63 cm^3 K mol^{-1} at 2 K. A reliable fit of the experimental data is not possible because of the overparametrization imposed by the asymmetry of this compound. In addition, it may have several triangular interactions that can give rise to competitive or frustrated interactions, giving a complicated set of superexchange pathways. A qualitative analysis of the $\chi_M T$ vs T plot indicates an overall antiferromagnetic interaction. The shape of the curve and the $\chi_M T$ value at low temperatures suggest a ground state close to a frustration point between the $S = 0$ spin level and at least one of the $S = 1$ spin levels. This fact is corroborated by the magnetization measurement performed at 2 K, which tends to a value close to only one electron under a field of 5 T. Trials to fit the experimental data with an oversimplified 3J model give multiple mathematical minima and poorly reasonable J values despite the good simulation of the experimental data (see the Supporting Information).

The value of the $\chi_M T$ product for **2** decreases gradually upon cooling (4.07 cm^3 K mol^{-1} at 300 K) until ca. 100 K, and below this temperature, it decreases quickly down to a value of 0.13 cm^3 K mol^{-1} at 4 K. This behavior is consistent with dominant antiferromagnetic interactions and an $S = 0$ ground state; the latter is corroborated by the appearance of a maximum in χ_M at 18 K.

Inspection of the molecular structure reveals that there are only two exchange parameters between the metal centers. The first one (J_1) is associated with the Ni1···Ni2 and Ni3···Ni4 interactions through two oximato μ-O atoms and one carboxylato bridge and the second one (J_2) with the Ni1···Ni3, Ni1···Ni4, Ni2···Ni3, and Ni2···Ni4 interactions, each involving two diatomic oximate groups. Best-fit[15] parameters employing the spin Hamiltonian $H = -J_1(S_1S_2 + S_3S_4) - J_2(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4)$ are $J_1 = -2.7$ cm^{-1}, $J_2 = -12.1$ cm^{-1}, and $g = 2.11$. The weak antiferromagnetic interaction J_1 agrees with the expected value for Ni−O−Ni bond angles around 94°, whereas J_2 is a normal value for Ni−oximato−Ni bridges.[6,16]

The $\chi_M T$ product for **3** decreases gradually from a value of 8.19 cm^3 K mol^{-1} at 300 K until a minimum of 5.50 cm^3 K mol^{-1} at 40 K. Below this temperature, the $\chi_M T$ product increases slightly and finally decreases because of zero-field-splitting and/or intermolecular interactions. The shape of the curve and the $\chi_M T$ values indicate an overall antiferromagnetic or ferrimagnetic behavior with a ground state greater than $S = 0$ (Figure 4). Magnetization measurements clearly indicate an $S = 3$ ground state (Figure 4, inset). Compound **3** exhibits five kinds of interactions; four of them are clearly different in nature involving the azido bridge (J_1), one diatomic oximate bridge (J_2), the double diatomic oximate/μ-O bridge (Ni−O−Ni = 110.2°; J_3), and the double μ−O/carboxylate bridge (Ni−O−Ni = 125.3°; J_4). We refrain from presenting here the very good (and magnetically reliable) fit of the data employing the appropriate 4J spin Hamiltonian because this leads to overparameterization; our efforts appear in the Supporting Information. Trials to simplify the fit with a 3J model, assuming $J_2 = J_3$, did not give good fits.

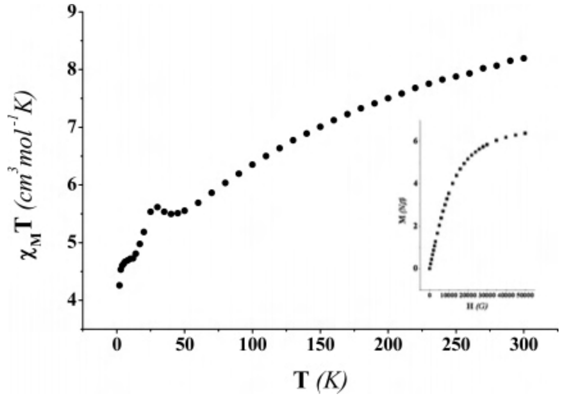

Figure 4. Plot of $\chi_M T$ vs T for **3**. The inset illustrates the reduced magnetization vs field plot, which tends to a value close to six unpaired electrons under a field of 5 T at 2 K.

In summary, the use of the $(py)_2CNO^-/MeCO_2^-$ "blend" has provided three new Ni clusters with interesting structures. The nuclearity of the cluster, $[Ni_4]$ to $[Ni_7]$, is controlled partly by the presence or absence of an extra inorganic anion and by the identity of this anion. The combination of $(py)_2CNOH$, carboxylate, and azide ligands with a host of other 3d transition elements or combinations of 3d with 4d, 5d, and 4f metals promises to deliver many new and exciting clusters.

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Supporting Information Available: Full synthetic procedures and elemental analyses of complexes **1**−**3**, the cores and the coupling schemes of **1**−**3**, $\chi_M T$ vs T and M vs H for complex **1**, $\chi_M T$ vs T and χ_M vs T plots for complex **2**, fit details for the three clusters (in a textual form), and crystallographic data for **1**·$0.5Me_2CO$·$3.2H_2O$, **2**·2.2MeOH·**1**·$7H_2O$, **3**·2MeCN·$12.2H_2O$ (CCDC Nos. 622481, 622480, and 622482, respectively) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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