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High-Spin M^{2+} Carboxylate Triangles from the Microwave

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The reaction of $M(O_2CMe)_2 \cdot 4H_2O$ (M = Ni, Co) with NaN_3 in pyridine/MeOH under microwave irradiation and controlled pressure/temperature leads to the formation of the trimetallic species $[M_3(N_3)_3(O_2CMe)_3(py)_5]$ (M = Ni, **1**; Co, **2**) in 4 min and in high yields. Both complexes display dominant ferromagnetic interactions and high-spin ground states.

One of the most challenging aspects for synthetic inorganic chemists is the development of new preparative routes for the synthesis of molecules under nonambient conditions as a means of exploring and widening the potential of individual reaction systems. Although the vast majority of polynuclear transition-metal clusters have been isolated under ambient reaction conditions,[1] an increasing number of complexes have been synthesized via the use of heat and pressure. Solvothermal techniques have recently been shown to be an excellent method for the synthesis of polymetallic clusters, not simply of inert metal ions such as Cr^{3+} but also of Mn^{3+}, Fe^{3+}, and Ni^{2+}.[2] We have recently embarked on a project to extend this idea even further by examining whether microwave heating can be used as an alternative method toward the formation of polynuclear metal complexes under controlled heat and pressure. Microwave heating is used widely in many areas of chemistry ranging from analytical chemistry and solid-state reactions to liquid-phase organic synthesis,[3–5] but surprisingly it has rarely been employed in liquid-phase inorganic synthesis. From our preliminary results,[6,7] we believe that it can provide a clean, cheap, and convenient method of heating that can result not only in higher yields and shorter reaction times but also in the formation of completely new products. Indeed, here we demonstrate the microwave-assisted synthesis of Ni_3 and Co_3 complexes that cannot be synthesized under ambient or solvothermal conditions.

The reaction between $Ni(O_2CMe)_2 \cdot 4H_2O$ and 1 equiv of NaN_3 in pyridine/MeOH under microwave irradiation (T = 120 °C; power = 250 W; pressure = 130 psi) for 4 min affords green crystals of $[Ni_3(N_3)_3(O_2CMe)_3(py)_5]$ (**1**) in yields of ~55%. The analogous procedure using $Co(O_2CMe)_2 \cdot 4H_2O$ gives pink crystals of $[Co_3(N_3)_3(O_2CMe)_3(py)_5]$ (**2**) in ~40% yield.[8] The lower yield for **2** can be attributed to the formation of a small amount of dark-brown crystals that form upon prolonged standing; these were crystallographically identified as the mononuclear species $[Co^{III}(N_3)_3(py)_3]$ (**3**).[9] Repeating the reactions that produced **1** and **2** under (a) ambient conditions and (b) solvothermal conditions yielded no isolable products in either case despite changes in reaction times, solvents, and temperatures.

Complex **1** crystallizes in the monoclinic space group $P2_1/n$ (Figure 1). The core of the molecule contains three Ni^{II} ions arranged in an isosceles triangle bridged via a central

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(8) Complex **1** analyzed (C, H, N) as **1**, expected (found): C, 42.56 (42.44); H, 3.92 (3.78); N, 22.42 (22.55). Diffraction data were collected with Mo Kα X radiation (λ = 0.710 73 Å) on a Bruker Smart APEX diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150 K. Crystal data: $C_{31}H_{34}N_{14}Ni_3O_6$, Z = 4, M = 874.83, turquoise blocks, monoclinic, $P121/n1$, a = 10.5737(3) Å, b = 13.7069(4) Å, c = 25.3967(7) Å, β = 100.352(2)°, V = 3620.90(18) Å^3, 37 308 reflections collected of which 10 312 were independent (R_{int} =0.053), 487 parameters and 0 restraints, R1 = 0.0618 [based on $F > 4\sigma(F)$], wR2 = 0.1797 (based on F^2 and all data). Complex **2** analyzed (C, H, N) as **2**, expected (found): C, 42.56 (42.48); H, 3.92 (3.81); N, 22.42 (22.58). Diffraction data were collected with Mo Kα X radiation (λ = 0.710 73 Å) on a Bruker Smart APEX diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150 K. Crystal data: $C_{31}H_{34}N_{14}Co_3O_6$, Z = 4, M = 875.50, pink blocks, monoclinic, $P121/n1$, a = 10.6450(2) Å, b = 13.7150(3) Å, c = 25.4911(5) Å, β = 100.113(10)°, V = 3663.78(13) Å^3, 37 784 reflections collected of which 9574 were independent (R_{int} = 0.033), 487 parameters and 0 restraints, R1 = 0.0343 [based on $F > 4\sigma(F)$], wR2 = 0.0741 (based on F^2 and all data).

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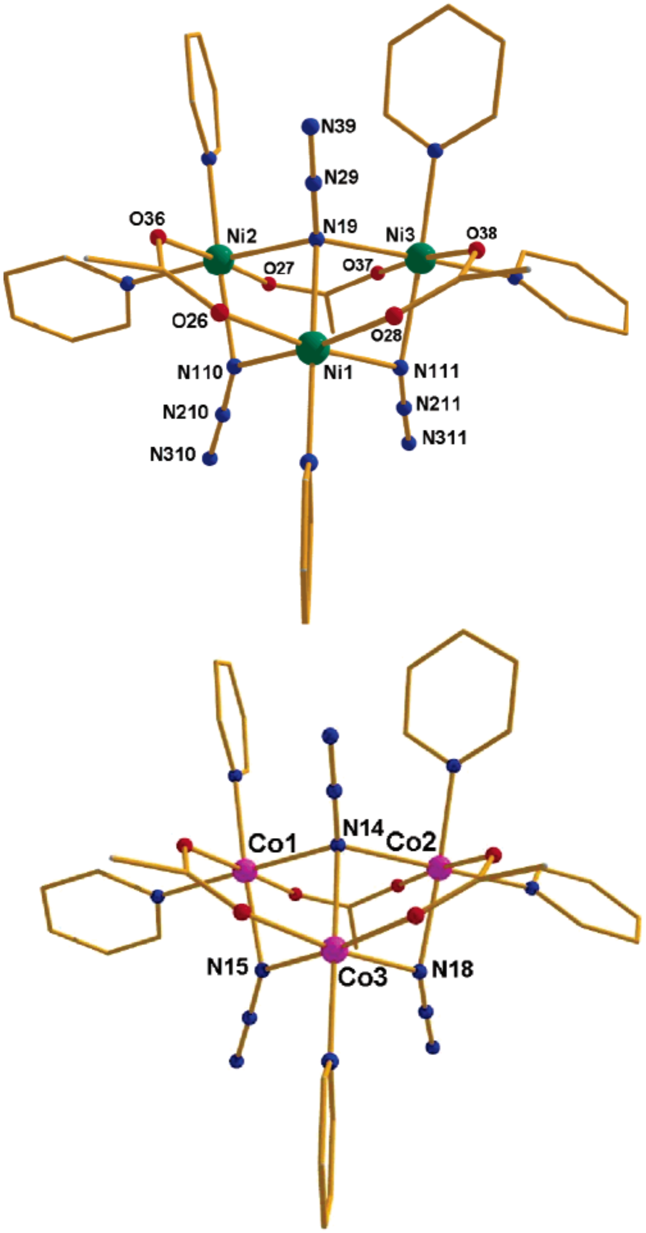

Figure 1. Molecular structures of complexes **1** (top) and **2** (bottom).

end-on μ_3-N_3^- ion [Ni1−N19−Ni3, 92.4(2)°; Ni1−N19−Ni2, 92.2(2)°; Ni3−N19−Ni2, 126.9(1)°] with Ni···Ni distances of 3.1 Å (Ni1···Ni2 and Ni1···Ni3) and 3.8 Å. Ni1 is further connected to the two basal Ni ions (Ni2 and Ni3) via two end-on μ-N_3^- ions [Ni1−N111−Ni3, 94.1(3)°; Ni1−N110−Ni2, 96.5(3)°] and two η^1:η^1:μ-O_2CMe ligands. Ni2 and Ni3 are bridged by one η^1:η^1:μ-O_2CMe ligand in addition to the central azide. The coordination of the metal ions is completed by the presence of five terminal pyridine molecules: two each on Ni2 and Ni3 and one on Ni1. All three Ni ions are six-coordinate and adopt distorted octahedral geometries with cis and trans angles in the ranges 84−96° and 172−179°, respectively. Complex **2** also crystallizes in the monoclinic space group $P2_1/n$, and its structure (Figure 1) is analogous to that of **1**. All three Co ions are in the 2+ oxidation state, as evidenced by bond valence summation calculations, charge balance considerations, and the presence of typical bond lengths for Co^{II} ions.

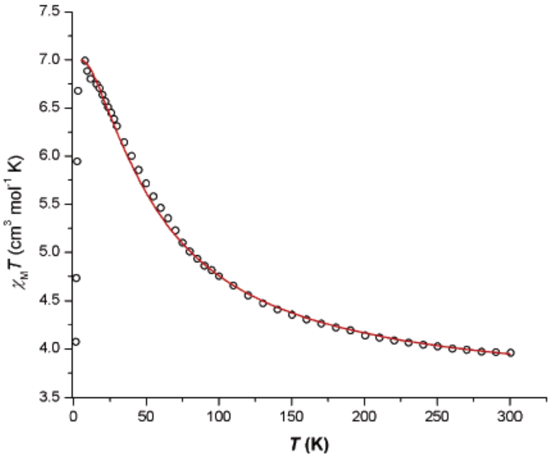

Figure 2. Plot of $\chi_M T$ vs T for complex **1**. The solid line represents a fit of the data in the temperature range 5−300 K (see the text for details).

Both complexes can be considered as M^{II} analogues of the well-known "M^{III} basic carboxylates" of general formula $[M_3O(O_2CR)_6(L)_3]^+$ (M = V, Cr, Mn, Fe, Co; L = py, H_2O, MeCN, etc.), whose structures consist of oxo-centered metal triangles. Here, the compensation of charge is achieved by replacing (a) the central μ_3-O^{2-} ion with a central μ_3-N_3^- ion and (b) three of the six bridging carboxylates with a combination of two μ-N_3^- ions and two additional terminal pyridines.

Variable-temperature dc magnetic susceptibility data were collected for both complexes in the temperature range 5−300 K in an applied field of 1.0 kG. The magnetic data for **1** are presented as $\chi_M T$ vs T in Figure 2. The $\chi_M T$ product increases upon cooling from a value of ~3.9 cm^3 K mol^{-1} at 300 K to a maximum value of ~7.0 cm^3 K mol^{-1} at 6 K, before falling rapidly below this temperature. The low-temperature maximum is indicative of an $S = 3$ ground state (with $g = 2.16$) and suggests the presence of dominant ferromagnetic exchange.[10] The decrease in $\chi_M T$ below 6 K is assigned to either zero-field splitting within the ground state, Zeeman effects, or intermolecular antiferromagnetic interactions. Inspection of the molecular structure reveals that two main exchange pathways exist (Figure 3): J_1, the interaction between Ni1···Ni2 and Ni1···Ni3 mediated by one μ-N_3^-, one η^1:η^1:μ-O_2CMe and one μ_3-N_3^-, and J_2, between Ni2···Ni3 mediated by one η^1:η^1:μ-O_2CMe and one μ_3-N_3^-. Using the program MAGPACK[11] and employing the spin Hamiltonian in eq 1 allowed us to satisfactorily model the data with the parameters $J_1 = +15.7$ cm^{-1}, $J_2 = -1.2$ cm^{-1}, and $g = 2.16$.

$$\hat{H} = -2J_1(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_1\cdot\hat{S}_3) - 2J_2(\hat{S}_2\cdot\hat{S}_3) \qquad (1)$$

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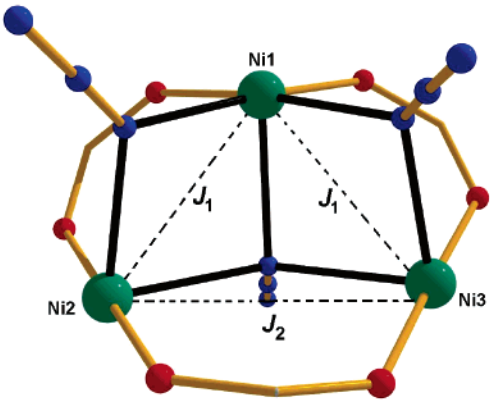

Figure 3. Core of complex **1** highlighting the two exchange interactions.

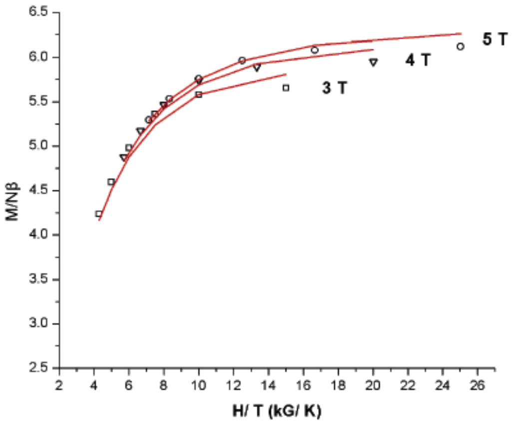

Figure 4. Plot of reduced magnetization ($M/N\beta$) vs H/T for complex **1** in the field and temperature ranges 30−50 kG and 2−7 K. The solid lines correspond to the fit of the data (see the text for details).

The magnitudes of the exchange interactions are in agreement with those previously reported for $\mathrm{Ni^{II}}$ complexes containing end-on μ- or μ_3-N_3^- bridges.[12]

To determine the spin ground state for complex **1**, magnetization data were collected in the ranges 10−50 kG and 2.0−7.0 K, and these are plotted as reduced magnetization ($M/N\beta$) vs H/T 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 (DS_z^2) and the Zeeman interaction, and carries out a full powder average. The corresponding Hamiltonian is given by eq 2, where D is the axial anisotropy, μ_B is the Bohr

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

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 $S = 3$, $g = 2.18$, and $D = +0.67$ cm^{-1} and was obtained using only the high-field ($H = 30{-}50$ kG) data. Incorporation of the low-field data in the fit afforded unreasonable parameters, while the corresponding fit with $D = -0.67$ cm^{-1} was of significantly poorer quality.

Upon cooling from room temperature, the $\chi_M T$ product for complex **2** (Figure SI1 in the Supporting Information) decreases, reaches a minimum value of ~9.5 cm^3 K mol^{-1} at 47 K, and then increases to reach a value of 13.2 cm^3 K mol^{-1} at ~6 K. This is again indicative of dominant ferromagnetic exchange between the metal centers. In octahedral symmetry, high-spin $S = {}^3/_2$ $\mathrm{Co^{II}}$ ions have an orbitally degenerate $^4T_1$ ground electronic term. Lowering of symmetry and spin−orbit coupling splits these into six Kramers doublets, and at low temperatures only one Kramers doublet corresponding to an effective spin $S' = {}^1/_2$ is populated. The exchange can thus be considered to occur between effective $S' = {}^1/_2$ states.[13] The initial decrease in $\chi_M T$ observed upon cooling from 300 K is due to the presence of spin−orbit coupling, while the increase below 47 K is due to the presence of ferromagnetic exchange between anisotropic $S' = {}^1/_2$ Kramers doublets. Magnetization data collected in the ranges 10−50 kG and 2.0−7.0 K (Figure SI2 in the Supporting Information) reveal that saturation is almost reached with a value of $M/N\beta \approx 8.4$ corresponding to an effective spin of the cluster $S' = {}^3/_2$ with a large anisotropic g' value.[14,15] This is consistent with the $\chi_M T$ value at low temperature and confirms the presence of dominant ferromagnetic exchange between the $\mathrm{Co^{II}}$ ions. A more detailed magnetic study of both complexes including multifrequency EPR will be reported in a full paper.

In conclusion, the synthesis of stable high-spin $\mathrm{M^{II}}$ carboxylate triangles similar to the well-known "$\mathrm{M^{III}}$ basic carboxylates" has been achieved via the use of microwave heating. The complexes cannot be prepared under ambient or solvothermal reaction conditions, suggesting that the use of microwave irradiation can provide cluster chemists with a new, fast, and powerful synthetic tool in the search for novel coordination compounds.

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Supporting Information Available: Crystallographic data for complexes **1** and **2** in CIF format and magnetic data for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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