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Two Chiral Metal Clusters Derived from Nucleophilic Addition of L-proline to Di-2-pyridyl Ketone

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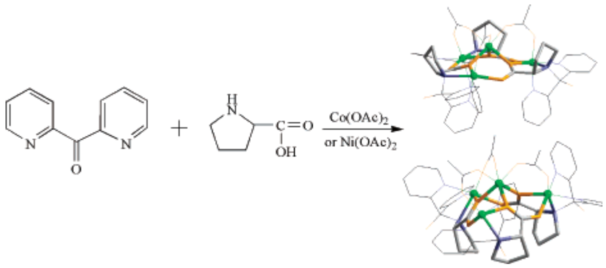
In the presence of cobalt (nickel) acetate, a chiral tetrahedral intermediate ligand of (*S*)-$(C_5NH_4)_2C(OH)(C_4NH_7CO_2H)$ was first formed from the nucleophilic addition of L-proline as a secondary amine to ketone (di-2-pyridyl ketone). Based on the ligand synthesized in situ, two chiral tetranuclear isomorphous complexes **1** and **2** with the formula $\{Na[M_4L_3(OAc)_3](ClO_4)_{1.5}(H_2O)_{1.5}\}(ClO_4)(OH)_{0.5}\cdot 3H_2O$ (M = Co, Ni) have been achieved. The Co_4 cluster (**1**) behaves as a ferromagnet.

The utility of certain metal salts in organic synthesis has been recognized to a great extent, and metal salts are found to play an important role in some amination, cyclization, hydration, and addition reactions.[1] In fact, the introduction of metal salts to some organic reactions provides efficient synthetic pathways for synthesizing novel molecules and makes some difficult or even impossible reactions possible. Furthermore, the reactions are also helpful for stabilizing some unstable intermediates, which are important for studying the reaction mechanism. Recently, many hydrothermal reactions show that many complexes or coordination polymers with novel structures can be synthesized through a simple one-pot reaction, which involves metal-assisted in situ ligand synthesis.[2] All of these show that the investigation of metal-assisted reactions is interesting and promising.

The reaction involving a nucleophilic addition of a secondary amine to ketone, in organic synthetic chemistry, usually, is the first step of successive reactions. The corresponding tetrahedral carbinolamines are commonly unstable and follow a dehydration reaction with enamines as the final products. Additionally, some tetrahedral carbinolamines have been observed in cyclic nucleophilic additions,[3] but similar examples are very rare in acyclizations.[4] In our work, we employed L-proline as a nucleophilic agent to react with di-2-pyridyl ketone (dpk) to synthesize a new ligand. The chiral tetrahedral intermediate (*S*)-HL [HL = $(C_5NH_4)_2C(OH)(C_4NH_7CO_2H)$] synthesized in situ was trapped by Co^{II} or Ni^{II} to form two new isomorphous chiral tetranuclear complexes **1** and **2** with the formula $\{Na[M_4L_3(OAc)_3](ClO_4)_{1.5}(H_2O)_{1.5}\}(ClO_4)(OH)_{0.5}\cdot 3H_2O$ (Scheme 1). Unfortunately, however, the chiral intermediate could not be isolated. Complexes **1** and **2** present a rare flattened tetrahedral metal skeleton. This is the first report of tertiary carbinol derived from metal-assisted nucleophilic addition of a secondary amino acid to ketone, which provides a new synthetic route to tertiary carbinol complexes,[5] as well as insight into chiral secondary amino acid derivatives.

Scheme 1



Reactions of metal acetate, L-proline, and dpk at 100 °C gave the crystals of the isomorphous complexes **1** and **2**.[6]

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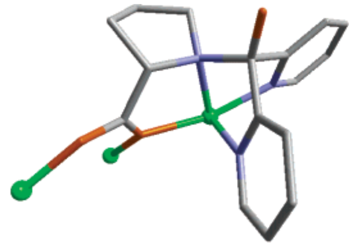
Single-crystal structural analyses reveal that the two complexes crystallize in the cubic space group $P2(1)3$.[7] They are comprised of two types of discrete clusters, $Na(H_2O)_3[\alpha\text{-}M_4L_3(OAc)_3]$ and $Na(ClO_4)_3[\beta\text{-}M_4L_3(OAc)_3]$ (Figure S1, Supporting Information), isolated perchlorate anions, an OH^- anion, and free water molecules, in which two chiral M_4 conformational isomers dominate. In each isomer, the metal skeleton may be described as a flattened tetrahedron with a 3-fold axis passing through the apex M^{II} atom and the basal center. Therefore, three basal M^{II} atoms are equivalent by C_3 symmetry. The basal edges (5.36−5.45 Å) determined by the three equivalent M^{II} atoms are much longer than the side edges (3.31−3.50 Å). This conformation is very rare in tetranuclear Co/Ni clusters and different from the documented tetrahedral (trigonal-pyramidal)[8] or triangular planar geometry.[9a] The four octahedral M^{II} atoms are perfectly held together by three $\mu_3{:}\eta^1{:}\eta^2\text{-}CH_3CO_2^-$ ions and three $\mu_3{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1\text{-}L^-$ ligands (Chart 1). The chiral ligand L^- holds an *S* conformation, in which the alkoxo O atom not attached to the metal centers remains protonated. The striking difference between the α and β isomers is that in the former the five-membered ring of the ligand locates on the same side of the apex according to the base, while in the latter it is on the other side of the apex (Figure 1).

Chart 1. Coordination Modes of the Ligand to the Metals[a]



[a] Cyan balls represent the metal ions; orange centers represent O atoms; blue centers represent N atoms.

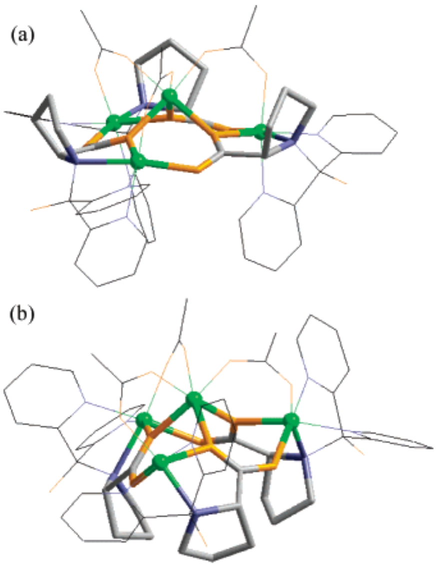


Figure 1. (a) α isomer. The five-membered ring of the ligand is located on the same side of the apex according to the base. (b) β isomer. The five-membered ring of the ligand is on the other side of the apex. (Cyan balls represent the metal ions; orange centers represent O atoms; blue centers represent N atoms.)

Magnetic measurements show that the two complexes exhibit different behaviors. Temperature-dependent magnetic susceptibility of **1** was measured at different external fields from 1 to 20 kG (Figure 2a). At a 5-kG field, upon cooling, χ_mT continuously decreases from 11.62 $cm^3\ mol^{-1}$ K (300 K) to 8.64 $cm^3\ mol^{-1}$ K (12 K), where a round minimum is observed. With further cooling, χ_mT increases to reach a maximum value of 8.85 $cm^3\ mol^{-1}$ K at about 5 K and then decreases quickly. The decrease is due to spin−orbit coupling of Co^{II} or antiferromagnetic coupling, while the increase corresponds to a ferromagnetic interaction. However, upon increasing external magnetic fields, the maximum becomes broader and lower and disappears finally (at 20 kG). By contrast, the maximum increases, with magnetic fields decreasing (at 1 kG). The behavior is identical with that of $Na_{12}[WCo_3(D_2O)_2(ZnW_9O_{34})_2]\cdot 40D_2O$.[10] In addition, the saturation moment (M_s) is about 8.4 $N\beta$ (Figure 2a, inset), which is consistent with an effective value for $S'_{cluster}$ of 2

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(6) ***Caution!** Perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.* **$\{Na[Co_4L_3(OAc)_3](ClO_4)_{1.5}(H_2O)_{1.5}\}(ClO_4)(OH)_{0.5}\cdot 3H_2O$ (1).** To a solution of CH_2Cl_2 (20 mL) were added dpk (0.1840 g, 1 mmol), L-proline (0.1151 g, 1 mmol), and $Co(OAc)_2\cdot 4H_2O$ (0.4981 g, 2 mmol), and the reaction mixture was refluxed for about 1 h. To the resulting red solution was added $NaClO_4\cdot H_2O$ (0.2101 g, 1.5 mmol), leading to the formation of a great deal of pink precipitation. After filtration, slow evaporation of the filtrate for about 2 weeks gave the red prism crystals of compound **1** (0.045 g, yield 8.1% based on dpk). Anal. Calcd for $C_{54}H_{66.5}Cl_{2.5}Co_4N_9NaO_{30}$: C, 38.86; H, 4.02; N, 7.55. Found: C, 38.52; H, 4.19; N, 7.22. IR (KBr pellet, cm^{-1}): ν(OH, H_2O) 3435, 3216, $\nu(COO^-)$ 1622, ν(C−OH) 1608, ν(py) 1446, 1441, 1382, 1021, 777, 763, 683, 664, $\nu(ClO_4^-)$ 1109, 1087, 625. **$\{Na[Ni_4L_3(OAc)_3](ClO_4)_{1.5}(H_2O)_{1.5}\}(ClO_4)(OH)_{0.5}\cdot 3H_2O$ (2). 2** was prepared following the same procedure as that for **1**, except for the replacement of CH_2Cl_2 (20 mL) and $Co(OAc)_2\cdot 4H_2O$ (0.4981 g, 2 mmol) with a 20-mL CH_3CH_2OH/H_2O solution (3:1, v/v) and $Ni(OAc)_2\cdot 4H_2O$ (0.4976 g, 2 mmol). After 2 weeks, the blue crystals of **2** were obtained (0.2511 g, yield 45.2% based on dpk). Anal. Calcd for $C_{54}H_{66.5}Cl_{2.5}N_9NaNi_4O_{30}$: C, 38.88; H, 4.02; N, 7.56. Found: C, 38.68; H, 4.26; N, 7.37. IR (KBr pellet, cm^{-1}): ν(OH, H_2O) 3428, 3208, $\nu(COO^-)$ 1622, ν(C−OH) 1605, ν(py) 1463, 1448, 1394, 1019, 777, 765, 684, 668, $\nu(ClO_4^-)$ 1108, 1088, 625.

(7) Crystal data for **1**: $C_{54}H_{66.5}Cl_{2.5}Co_4N_9NaO_{30}$, cubic, space group $P2(1)3$, $a = 23.917(3)$ Å, $V = 13681(3)$ Å^3, $Z = 8$, $D_c = 1.621$ g cm^{-3}, Mo Kα, $\lambda = 0.710\,73$ Å, 87 132 reflections, 8099 independent reflections ($R_{int} = 0.0484$), Flack parameter 0.01(2), R1 = 0.0671, and wR2 = 0.1841. Crystal data for **2**: $C_{54}H_{66.5}Cl_{2.5}N_9NaNi_4O_{30}$, cubic, space group $P2(1)3$, $a = 23.8703(8)$ Å, $V = 13601.1(8)$ Å^3, $Z = 8$, $D_c = 1.629$ g cm^{-3}, Mo Kα, $\lambda = 0.710\,73$ Å, 106 428 reflections, 10 373 independent reflections ($R_{int} = 0.0633$), Flack parameter 0.06(2), R1 = 0.0729, and wR2 = 0.2012. X-ray single-crystal data were collected at 130(2) K on a Mercury CCD area detector diffractometer. These structures were solved by direct methods and were refined by full-matrix least-squares methods using *SHELXL-97*.[13] CCDC Nos. 297403 and 297404.

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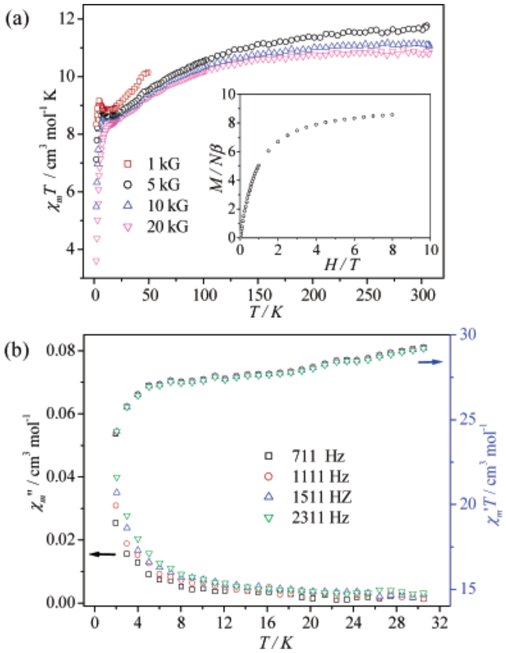


Figure 2. For **1**. (a) Plots of $\chi_m T$ vs T upon different magnetic fields (inset: field dependence of the magnetization at 2 K). (b) Plots of the temperature dependence of ac susceptibility: the in-phase $\chi_m'T$ and the out-of-phase χ_m'' at a 3-Oe field.

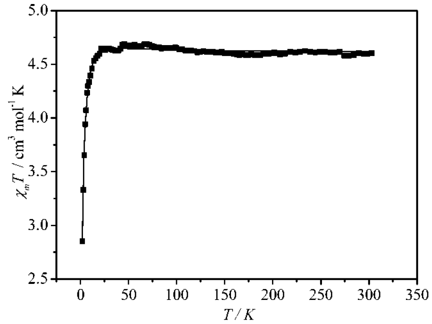
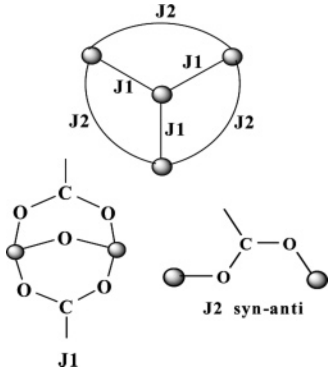


Figure 3. Plot of $\chi_m T$ vs T for **2**. The continuous line presents the best fit, while the black points present the experimental data.

and an average $g > 3$ for the Co_4 cluster. The ac susceptibility shows that there are frequency-dependent out-of-phase signals χ_m'' in the 8−2 K range but no χ_m'' peak appears, similar to the literature reported (Figure 2b).[11]

Temperature-dependent magnetic susceptibility of **2** was measured in the range of 2−300 K at 5 kG (Figure 3). The dc $\chi_m T$ value remains almost constant (about 4.61 cm^3 mol^{-1} K) from 300 to 20 K, close to the expected value for four noninteracting Ni^{II} centers with $S_i = 1$ and $g = 2.3$.[12] This behavior suggests a weak intermolecular interaction. Then $\chi_m T$ drops sharply to 2.85 cm^3 mol^{-1} K at 2 K. Taking into account the geometry of Ni^{II} ions, two exchange parameters J_1 and J_2 relating with the neighboring spins are suggested (Chart 2). Considering both isotropic exchange interactions and an axial single ion anisotropy of the type DS_{iz}^2, a fit was carried out with Hamiltonian $H = -2J_{ij}\sum S_iS_j + DS_{iz}^2$ by applying the *MAGPACK* program.[8a,9] The best-fit parameters obtained from this computing model are $J_1 = -1.86$ cm^{-1}, $J_2 = 2.12$ cm^{-1}, $D = 3.53$ cm^{-1}, $g = 2.15$, and $R = 2.12 \times 10^{-5}$. All parameters seem to be logical, and the values of D and g can be compared with those of the literature.[9a,b] In addition, we have also adopted other parameter sets to fit the magnetic susceptibility data (Supporting Information).

Chart 2. Magnetic Exchange Pathways for **2**



In summary, in the presence of cobalt (nickel) acetate, a chiral intermediate derived from the nucleophilic addition of L-proline as a secondary amine to ketone (dpk) has been first synthesized in situ, which provides a new strategy for the syntheses of tertiary carbinol compounds. Two chiral Co/Ni clusters bearing a rare flattened tetrahedral configuration have been obtained with the chiral intermediate as a ligand. Interestingly, the Co_4 cluster acts as a ferromagnet, different from the Ni_4 cluster.

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Supporting Information Available: X-ray crystallographic data (CIF) and supplementary figures from magnetic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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