# Metal Directed One-Pot Syntheses: Mono-, Di- and Tetra-nuclear Clusters [1]

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Upon reaction of HL<sup>1</sup> 1 (picoline-tetrazolylamide) with cobalt(II) acetate under aerobic conditions or with copper(II) acetate, the mono-nuclear complex  $[Co^{III}(L^1)_3]$  3 and the di-nuclear complex  $[Cu_2(L^1)_4]$  4 were generated. In 3 and 4,  $(L^1)^-$  exclusively coordinates across its nitrogen donors. However, when HL<sup>2</sup> 5 (picoline-tetrazolyl*thio*amide) was reacted with copper- or nickel acetate, the di-nuclear cluster  $[Cu_2(L^2)_4]$  6 and the tetra-nuclear cluster  $[Ni_4(L^2)_8]$  7, respectively, were isolated. Contrary to 3 and 4, in 6 and 7,  $(L^2)^-$  also coordinates across sulfur.

Key words: Cluster Compounds, Self Assembly, Supramolecular Chemistry

#### Introduction

Recent developments in the field of design and synthesis of supramolecular inorganic structures exhibiting novel properties have provided exciting new prospects [2]. In this context, we reported on rectangular tetra-nuclear clusters  $[M_4(L^1)_8]$  **2**, which were accessible in a one-pot reaction from zinc- or nickel acetate and picoline-tetrazolylamide HL<sup>1</sup> **1** (Scheme 1) [3]. The magnetic susceptibility of powder samples of **Ni-2** (R = Et) showed temperature dependence. With decreasing temperature  $\chi T$  increases, which can only be explained by an intramolecular ferromagnetic coupling of the nickel ions. These findings led us to further study the potential of  $(L^1)^-$  and similar ligands for the generation of novel oligo-nuclear chelate clusters.

## **Results and Discussion**

Upon reaction of  $HL^1$  **1** in methanol with cobalt(II) acetate under aerobic condition and work-up with diethylether the dark-red compound **3** was isolated. The FAB-MS spectra of solid **3** showed signals corresponding to  $[Co(L^1)_3]$ , indicating an aerobic oxidation of Co(II) to Co(III). When diethylether was allowed to diffuse into a solution of **3** in dichloromethane/methan-



Scheme 1. Synthesis of  $[M_4(L^1)_8]$  2 from HL<sup>1</sup> 1.

ol, dark-red blocks, suitable for single crystal Xray diffraction analysis, were isolated. This study proved the formation of the mono-nuclear complex  $[Co^{III}(L^1)_3]$  **3** [4]. The central cobalt(III) ion is coordinated by six nitrogen donors stemming from the pyridine- and amide functions of each of the three ligands. The bond angles (Co—N) of the *mer*-stereoisomer **3** vary from 79.26° to 97.9°, resulting in a slightly distorted octahedral coordination sphere at cobalt (Scheme 2).

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Scheme 2. Syntheses and X-ray structures of  $[Co(L^1)_3]\,{\bf 3}$  and  $[Cu_2(L^1)_4]\,{\bf 4}$  from HL^1 1.

In contrast to the preferably octahedral coordination of Co(III) and Ni(II) ions, copper(II) often prefers penta-coordination. Therefore, reaction of copper(II) and HL<sup>1</sup> 1 should lead to complexes of a different type than  $[Ni_4(L^1)_8]$  Ni-2 or  $[Co^{III}(L^1)_3]$  3. Reaction of a methanolic copper(II) acetate solution with HL<sup>1</sup> 1, work-up and diffusion of diethylether in a methanolic solution of 4 lead to deep blue crystals suitable for X-ray analysis. According to this study, 4 is present in the crystal as the neutral di-nuclear chelate complex  $[Cu_2(L^1)_4]$ , in which the Cu(II) ions are coordinated by five nitrogen donors of two pairs of ligands. The two tridentate ligands link the two copper ions of the  $[Cu_2(L^1)_2]^{2+}$  core in such a way, that the pyridine- and amide nitrogen donors are coordinated to the same copper ion, while the tetrazolyl nitrogen donors are coordinated to the neighbouring ions. The second set of two additional bidentate ligands coordinates via the pyridine and the amide nitrogen donors only and completes the coordination spheres at the two copper ions. The distance between the copper ions is 2.618 Å. The bond angles (N—Cu—N) of 4 vary from 80.2° to 106.2°, resulting in a distorted squarepyramidal arrangement at copper (Scheme 2).

It is interesting to note, that in  $[M_4(L^1)_8]$  2 (M =  $Zn^{2+}$ , Ni<sup>2+</sup>) the bridging ligands (L<sup>1</sup>)<sup>-</sup> coordinate to these metal ions via their amide-oxygen donors. How-



Scheme 3. Syntheses and X-ray structures of  $[Cu_2(L^2)_4]$  6 and  $[Ni_4(L^2)_8]$  7 from HL<sup>2</sup> 5.

ever, in  $[Co(L^1)_3]$  **3** and  $[Cu_2(L^1)_4]$  **4** the ligands  $(L^1)^$ coordinate only via their nitrogen donors. These results prompted us to study the reaction products of the thioanalog  $HL^2$  5 of  $HL^1$  1 with thiophilic  $Cu^{2+}$ .  $HL^2$  5 was generated from  $HL^1$  **1** with Lawesson's reagent [5]. When a methanolic Cu(II) acetate solution was stirred with HL<sup>2</sup> 5, after a few hours a brown precipitate was isolated. Recrystallization of this material from a dichloromethane solution, layered with diethylether, afforded dark-green cuboids of  $[Cu_2(L^2)_4]$ 6 [6].  $[Cu_2(L^1)_4]$  4 and  $[Cu_2(L^2)_4]$  6 have identical elemental composition as shown by FAB mass spectrometry. In order to unequivocally determine the structure of 6, we carried out an X-ray crystallographic structure determination. According to the results of this analysis, in 6 each copper ion is coordinated by three nitrogenand two sulfur donors of two types of ligands, two tridentade bridging ligands and two bidentate ligands. The distance between the copper ions in 6 is 6.027 Å (Scheme 3).

Alike the rectangular tetra-nuclear clusters  $[M_4(L^1)_8]$  **2** (M=Zn<sup>2+</sup>, Ni<sup>2+</sup>), which were accessible in a one-pot reaction from the corresponding metal acetates and picoline-tetrazolyl*amide* HL<sup>1</sup> **1**,  $[Ni_4(L^2)_8]$ **7** was generated from picoline-tetrazolyl*thioamide* HL<sup>2</sup> **5** with nickel(II) acetate in methanol (Scheme 3).

	3	4	6	7
Formula	C24H21N18O3C0	C32H28N24O4Cu2	C36H36N24S4Cu2	C72H72N48S8Ni4
	$\cdot 2 CH_3OH$		$\cdot CH_2Cl_2$	· 4 CHCl <sub>3</sub>
$M_r$	732.60	939.86	1145.13	2578.57
Crystal size [mm]	$0.30 \times 0.30 \times 0.20$	0.40  imes 0.20  imes 0.20	0.40  imes 0.30  imes 0.20	$0.35 \times 0.30 \times 0.20$
Crystal system	triclinic	monoclinic	triclinic	tetragonal
Space group	$P\bar{1}$	C2/c	$P\overline{1}$	$I4_1/a$
<i>T</i> [K]	173(2)	133(2)	173(2)	173(2)
<i>a</i> [Å]	9.050(2)	22.982(5)	10.707(2)	23.419(3)
<i>b</i> [Å]	11.124(2)	9.819(3)	11.438(2)	23.419(3)
<i>c</i> [Å]	15.954(3)	17.932(4)	19.594(4)	20.346(4)
α [°]	88.94(3)	90	93.69(3)	90
β [°]	74.74(3)	107.86(2)	93.66(3)	90
γ[°]	70.38(3)	90	94.08(3)	90
<i>V</i> [Å <sup>3</sup> ]	1455.2(5)	3851.5(17)	2383.0(8)	1115.9(3)
Z	2	4	2	4
$P_{\text{calcd}}  [\text{Mgm}^{-3}]$	1.672	1.621	1.596	1.535
$\theta$ Range [°]	2.27 to 26.95	2.27 to 24.72	6.82 to 26.37	6.82 to 25.03
Reflections collected	5782	27139	15016	9355
Unique reflections	5475	3279	9434	4819
$[R_{int}]$	0.0243	0.0673	0.0223	0.0235
Refl. observed $[I > 2\sigma(I)]$	3891	2539	7370	4819
Parameters	535	282	622	334
Absorption correction method	Psi-scans	Semi-empirical	Psi-scans	Scalepack
Final $R1[I > 2\sigma(I)]$	0.0459	0.0348	0.0420	0.0723
wR2 (all data)	0.1482	0.0836	0.1259	0.2044
Largest residuals [e Å <sup>-3</sup>	0.538/-0.552	0.450/-0.315	0.939/-0.666	1.065/-1.175

Table 1. Details of X-ray structure determinations.

Single crystals of 7, suitable for X-ray structure analysis were obtained from a solvent cocktail (dichloromethane/methanol/diethylether) at 0 °C after three months. One of the main structural characteristics of the square  $[2 \times 2]$  grid 7 are the two different sets of bonding modes observed for  $(L^2)^-$ . One set of four tetradentate ligands links two nickel ions each in five-membered and six-membered chelate rings to construct the  $[Ni_4(L^2)_4]^{4+}$  core. In this case  $(L^2)^{-1}$ coordinates to one metal ion via the pyridine and the amide nitrogen donors and to the neighbouring metal ion via the nitrogen donor of the tetrazolyl group and the sulfur donor of the thioamide function. By contrast, the four ligands  $(L^2)^-$  of the second set exhibit a bidentate bonding mode. These ligands coordinate via the pyridine and the amide nitrogen donors only and complete the slightly distorted octahedral coordination sphere at the metal vertices. The distance between the nickel ions amounts to 5.560 Å.

The magnetic properties of  $[Ni_4(L^2)_8]$  7 turned out to be very similar to those of  $[Ni_4(L^1)_8]$  2. In both samples, magnetic coupling and anisotropy of single crystals were examined by magnetization measurements and in particular by high-field torque magnetometry at low temperatures. The data were analyzed in terms of an effective spin Hamiltonian appropriate for Ni(II) ions. In both compounds, we found a weak intramolecular ferromagnetic coupling of the four Ni(II) spins and sizeable single-ion anisotropy parameters of the easy-axis type [3,7].

## **Experimental Section**

*General techniques:* Metal salts and reagents were used as obtained from Aldrich. IR spectra were recorded from KBr pellets on a Bruker IFS 25 spectrometer. NMR spectra were recorded on a JEOL JNM-EX-400 spectrometer. FAB-MS spectra were recorded on a Micromass ZAB-Spec spectrometer. Elemental analyses were performed on a EA 1110 CHNS-Microautomat.

HL<sup>1</sup> (1): Cf. Lit. [3].

 $HL^2$  (5) [8]: A suspension of 2-ethyl-5-aminotetrazole (1.13 g, 10 mmol) and lithium chloride (1.0 g) in anhydrous *N*-methyl-pyrrolidin-2-one was cooled to 0 °C and 2-pyridyl chloride [8] (1.48 g, 10 mmol) was added. The reaction mixture was stirred for three days at 20 °C, 200 ml water was added and the microcrystallinic precipitate of picoline-tetrazolylamide was collected on a glass frit and crystallized from methanol. Subsequent reaction with Lawesson's reagent in toluene at 85 °C for 17 h, hydrolysis and purification by column chromatography (silica gel 60, ethyl

acetate/petroleum ether = 10:1) afforded **5**. Yield: 0.89 g (38%) orange cubes. – M. p. 101 °C. – IR(KBr): v = 3200, 3 080, 1 560, 1 043. – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.71$  (t, 3H, CH<sub>3</sub>); 4.74 (q, 2H, CH<sub>2</sub>); 7.53 (dd, 1H, Ar-H); 7.91 (dd, 1H, Ar-H); 8.58 (d, 1H, Ar-H); 8.74 (d, 1H, Ar-H); 12.53 (s, 1H, NH). – <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CDCl<sub>3</sub>):  $\delta = 14.35$  (CH<sub>3</sub>); 49.01 (CH<sub>2</sub>); 124.70, 126.58, 137.53, 146.68 (4 Ar-CH); 148.22 (1 Ar-C<sub>ipso</sub>); 160.75 (CN<sub>3</sub>), 189.47 (C=S). – MS (EI, 70 eV): m/z (%) = 234 (17) [M<sup>+</sup>]. – C9H<sub>10</sub>N<sub>6</sub>S (234.28): calcd. C 46.14, H 4.30, N 35.87, S 13.69; found. C 46.26, H 4.33, N 36.03, S 10.71.

# $[Co(L^1)_3]$ ( 3), $[Cu_2(L^1)_4]$ ( 4), $[Cu_2(L^2)_4]$ ( 6) and $[Ni_4(L^2)_8]$ ( 7)

*General method:* To a solution of the corresponding metal(II) acetate (0.5 mmol) in 30 ml of CH<sub>3</sub>OH was added a solution of HL<sup>1</sup> **1** or HL<sup>2</sup> **5** (1.0 mmol) in 20 ml of CH<sub>3</sub>OH. The reaction mixture was stirred at 20 °C for 2 h, concentrated to 20 ml and layered with 10 ml of diethyl ether. The precipitate was collected, dried under reduced pressure and crystallized.

 $[Co(L^1)_3]$  ( 3): Educt: HL<sup>1</sup> 1. Yield: 170 mg (85%) darkred blocks from methanol/dichloromethane/diethyl ether. – M.p. > 250 °C (decomp). – IR (KBr): v = 1643, 1605, 1568. – MS (FAB, 3-NBA): m/z (%): 669 (100)  $[CoL_3]^+$ . –  $C_{24}H_{21}N_{18}O_3Co$  (668.48): calcd. C 43.12, H 3.16, N 37.72; found. C 41.80, H 3.18, N 36.75.

 $[Cu_2(L^1)_4]$  (4): Educt: HL<sup>1</sup> **1**. Yield: 193 mg (82%) blue blocks from methanol/diethyl ether. – M.p. > 250 °C (decomp). – IR (KBr): v = 1641, 1551. – MS (FAB, 3-NBA): m/z (%): 734 (39)  $[Cu_2L_4]^+$ . –  $C_{32}H_{28}N_{24}O_4Cu_2$  (939.83): calcd. C 40.90, H 3.00, N 35.77; found. C 40.43, H 2.96, N 31.58.

 $[Cu_2(L^2)_4]$  (6): Educt: HL<sup>2</sup> 5. Yield: 270 mg (51%) darkgreen blocks from dichloromethane/diethyl ether. – M.p. >

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250 °C (decomp). – IR (KBr): v = 1633, 1556. – MS (FAB, 3-NBA): m/z (%): 1061 (4)  $[Cu_2L_4]^+$ . –  $C_{36}H_{36}N_{24}S_4Cu_2$  (1060.20): calcd. C 40.78, H 3.42, N 31.71, S 12.10; found. C 40.42, H 3.44, N 31.38, S 11.78.

 $[Ni_4(L^2)_8]$  (7): Educt: HL<sup>2</sup> **5**. Yield: 207 mg (79%) orange-brown blocks from chloroform/methanol/diethyl ether. – M.p. > 250 °C (decomp). – IR (KBr): v = 1556, 1505, 1449. – MS (FAB, 3-NBA): m/z (%): 2098 (4)  $[Ni_4(L^2)_8]^+$ . –  $C_{72}H_{72}N_{48}S_8Ni_4$  (2100.03): calcd. C 41.16, H 3.45, N 32.00, S 12.21; found. C 39.53, H 3.65, N 29.92, S 9.55.

Single-crystal X-ray structure analyses: Details for crystal data, data collection, and refinement are given in Table 1. X-ray data were collected on a Nonius Kappa CCD area detector (**3**, **6**, **7**) and on a Stoe-Siemens-Huber four circle diffractometer equipped with a CCD area detector (**4**) with Mo-K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods with SHELXS-97 [10] and refined with full-matrix least-squares against  $F^2$  with SHELXL-97 [11]. All non-hydrogen atoms were refined anisotropically.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-193557 (**3**), no. CCDC-193676 (**4**), no. CCDC-193558 (**6**), and no. CCDC-193559 (**7**). These data can be obtained free of charge via www.ccdc.cam.uk/const/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or email: deposit@ccdc.cam.ac.uk).

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