A Rectangular Zinc Cluster and a Rectangular Nickel Cluster That Exhibits Ferromagnetic Coupling[**]

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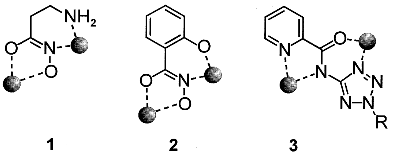
*Dedicated to Professor Siegfried Schneider
on the occasion of his 60th birthday*

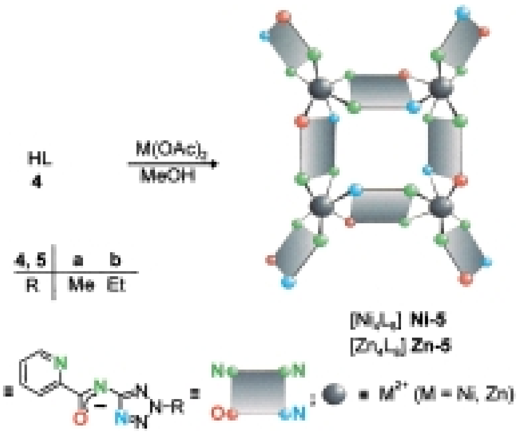
In the last few years the development of new concepts for the rational design of polynuclear clusters has led to considerable progress in supramolecular chemistry.[1] The use of carefully selected ligands and metal ions has allowed the construction of clusters with defined geometry and special properties. Particular interest has focused on the development of so-called single-molecule magnets.[2]

β-Alaninehydroxamic acid and salicylhydroxamic acid react with appropriate metal ions to give tetranuclear metallacoronates.[3] The cyclic linkage of the four metal ions is based on the building blocks **1** and **2**, which as a common feature exhibit a five- and a six-membered chelate ring (Scheme 1). Likewise, picoline-tetrazolylamides of the type HL **4** should also be suitable for the formation of four-membered metallacycles, provided, deprotonated **4** also fits the geometric conditions necessary to form the bischelate **3**, a structurally analogous module of **1** and **2**.



Scheme 1. Schematic representation of the commensurate building blocks **1**–**3** suitable for the construction of cyclic tetranuclear clusters.

In order to confirm this hypothesis, we treated **4b** with nickel(II) acetate in methanol. After work-up a violet solid was isolated. Based on the elemental analysis and FAB-MS spectrum, **Ni-5b** (*m/z* 1972) is a tetranuclear metal chelate complex of the composition $[Ni_4L^b_8]$ (Scheme 2).



Scheme 2. Synthesis of the tetranuclear nickel and zinc clusters $[M_4L_8]$ **5**.

For unequivocal characterization of $[Ni_4L^b_8]$ **Ni-5b** we carried out an X-ray crystallographic structure analysis.[4] According to this study, **Ni-5b** is present in the crystal as a square [2 × 2] grid ($d_{Ni-Ni} = 5.567$ Å, $\text{angle}_{Ni-Ni-Ni} = 84.40°$). One of the main structural characteristics of **Ni-5b** is the two different sets of bonding modes observed for $(L^b)^-$. A set of four tetradentate ligands links two nickel ions each through a five-membered chelate ring and a six-membered chelate ring leading to the construction of the $[Ni_4L^b_4]^{4+}$ core. In this case $(L^b)^-$ coordinates to one nickel ion through the pyridine and the amide nitrogen donors and to the neighboring nickel ion through the nitrogen donor of the tetrazolyl group and the oxygen donor of the amide function. In contrast, the four ligands $(L^b)^-$ of the second set exhibit a bidentate bonding mode. These ligands coordinate across the pyridine and the amide nitrogen donors only and complete the slightly distorted octahedral coordination sphere at the nickel vertices (Figure 1).

Two enantiomeric pairs ((Δ)-, (Λ)-*fac*, and (Δ)-, (Λ)-*mer*) are principally possible for octahedral complexes of the type MA_3B_3 (with bidentate ligands $M(AB)_3$).[7] The cluster $[Ni_4L^b_8]$ **Ni-5b** has idealized S_4 molecular symmetry and is thus achiral (($\Delta,\Lambda,\Delta,\Lambda$)-*fac,meso* form).

The zinc complex **Zn-5a** was obtained as a white solid in a similar manner to **Ni-5b**. Likewise, $[Zn_4L^a_8]$ **Zn-5a** is present in the crystal as a square [2 × 2] grid ($d_{Zn-Zn} = 5.657$ Å, $\text{angle}_{Zn-Zn-Zn} = 81.04°$) and is isostructural[8] with $[Ni_4L^b_8]$ **Ni-5b**. Additional characterization of **Zn-5a** by NMR spectroscopy was hindered by its poor solubility.

The temperature dependence of the magnetic susceptibility of powder samples of **Ni-5b** is shown as χT in Figure 2. With decreasing temperature χT increases. It is well known that for Ni^{II} ions ligand-field interactions lead to a zero-field splitting (ZFS) and thereby to a deviation from the Curie–law ($\chi T =$ constant) at low temperatures.[9, 10] However, regardless of the sign of the ZFS a decrease of χT is always expected (see Figure 2).[10] Therefore, the increase of χT can only be explained by an intramolecular ferromagnetic coupling of the Ni ions.

For a quantitative analysis of the magnetic properties of **Ni-5b** measurements at fields of 3, 10, 30, and 55 kG were all at once fitted to a model spin-Hamiltonian. The spin-Hamiltonian $\boldsymbol{H}_{ex} = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1)$, which solely takes into account a magnetic coupling, reproduced the data roughly. The additional inclusion of a ligand-field

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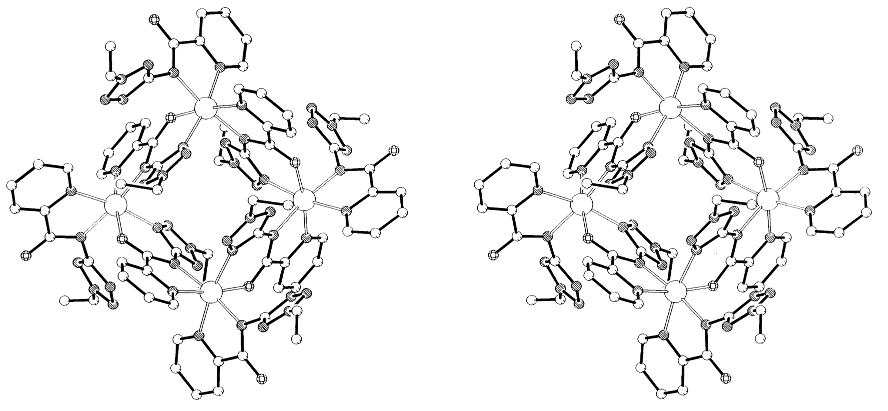

Figure 1. Molecular structure of **Ni-5b** in the crystal (PLUTON presentation). Stereoview perpendicular to the Ni_4 plane (along the S_4 axis); H atoms omitted for clarity. Carbon shaded, nitrogen hatched, oxygen chequered, nickel transparent. Selected bond lengths [Å] and angles [°] of tetradentate $(L^b)^-$: N(pyridine)-Ni 2.111(3), N(amide)-Ni 2.065(3), N(tetrazole)-Ni 2.062(3), O-Ni 2.032(2); N(pyridine)-Ni-N(amide) 79.26, N(tetrazole)-Ni-O 131.00.

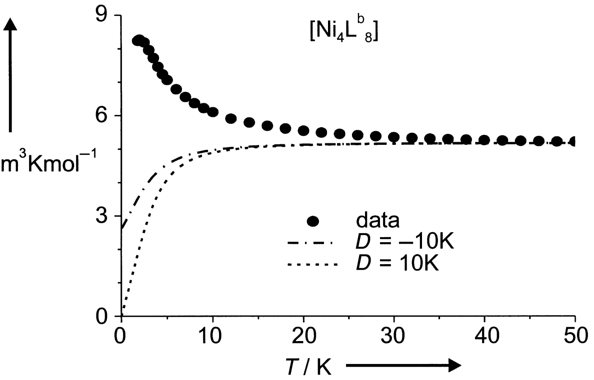

Figure 2. Temperature dependence of the magnetic susceptibility of **Ni-5b** as measured at a field of 3 kG. Dashed curves were calculated with the spin-Hamiltonian $\boldsymbol{H}_{ex} + \boldsymbol{H}_{ZFS}$ for $J = 0$ and $D = \pm 10$ K ($g = 2.24$).

interaction in the form of a uniaxial ZFS, $\boldsymbol{H}_{NFA} = D\sum_i \left(S_{i,z}^2 - \frac{2}{3}\right)$, led to excellent fits of the data with $|D| \approx 3$ K and $g = 2.24$. The sign of D could not be determined unambiguously from the powder measurements. However, regardless of the sign of D, we obtained ferromagnetic values for the coupling J ($J \approx 1.5$ K), in agreement with the above qualitative consideration.

Experimental Section

Ligand HL **4** was synthesized from 2-picolinyl chloride[11] and 2-alkyl-5-aminotetrazole[12] according to reference [13].

Ni-5b and **Zn-5a**: General procedure: A solution of HL **4** (1.0 mmol) in methanol (20 mL) was added to a solution of nickel(II) or zinc(II) acetate (0.5 mmol) in methanol (30 mL). The reaction mixture was stirred at 20°C for 2 h, concentrated to 20 mL, and layered with diethyl ether (10 mL). The precipitate was collected, dried under reduced pressure, and crystallized.

Ni-5b: Yield: 210 mg (85%) violet tetrahedrons (methanol/dichloromethane/diethyl ether 1:1:1); correct elemental analysis; decomp > 250°C; IR ($CHBr_3$): $\tilde{\nu} = 1620\ cm^{-1}$ (C=O), 1558 (C=C); FAB-MS (3-nitrobenzyl alcohol (3-NBA)): m/z (%): 1972 (6) $[Ni_4L^b{}_8]^+$.

Zn-5a: Yield: 193 mg (86%) colorless tetrahedrons (methanol/diethyl ether 1:1); correct elemental analysis; decomp >250°C; IR ($CHBr_3$): $\tilde{\nu} = 1610\ cm^{-1}$ (C=O), 1560 (C=C); FAB-MS (3-NBA): m/z (%): 741 (100) $[Zn_2L^a{}_3]^+$.

The magnetic moment of a powder sample of **Ni-5b** was measured with a commercial SQUID magnetometer (Quantum Design). Data were corrected for diamagnetic contributions and temperature independent paramagnetism (TIP).

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[4] Crystal structure analysis data for $[Ni_4L^b{}_8]$ **Ni-5b**: $C_{72}H_{72}N_{48}O_8Ni_4 \cdot 4CH_2Cl_2$, $M_r = 2312.32$; crystal dimensions: $0.30 \times 0.30 \times 0.20$ mm, tetragonal; space group $I4(1)/a$; $a = b = 22.8466(6)$, $c = 20.1411(1)$ Å, $V = 10513.0(5)$ Å^3; $Z = 8$; $F(000) = 4736$, $\rho_{calcd} = 1.461\ Mg\,m^{-3}$; diffractometer: Nonius KappaCCD; $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); $T = 173(2)$ K; graphite monochromator; measurement range: $6.95 \leq \theta \leq 24.98$; section of the reciprocal lattice: $-27 \leq h \leq 27$, $-19 \leq k \leq 19$, $-23 \leq l \leq 23$; of 8260 measured reflections, 4509 were independent, and 3436 with $I > 2\sigma(I)$; linear absorption coefficient 0.983 mm^{-1}. The structure was solved by direct methods using SHELXS-97 and refined with all data (326 parameters) by full-matrix least-squares on F^2 using SHELXL97;[5] all non-hydrogen atoms were refined anisotropically; $R_1 = 0.0533$ (observed reflections); $wR_2 = 0.1552$ (all data); max./min. residual electron density 0.758/ − 0.403 e Å^{-3}.[6]

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[6] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-140701 (**Ni-5b**), and CCDC-140702 (**Zn-5a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[8] Crystal structure analysis data for **Zn-5a**: $C_{64}H_{56}N_{48}O_8Zn_4 \cdot 4\,CH_3OH$, $M_r = 2011.20$; crystal dimensions: $0.30 \times 0.30 \times 0.15$ mm, tetragonal, space group $I\bar{4}$, $a = b = 14.251(2)$, $c = 21.302(2)$ Å, $V = 4326.3(9)$ Å^3, $Z = 8$, $F(000) = 2056$, $\rho_{calcd} = 1.544\ \mathrm{Mg\,m^{-3}}$; diffractometer: Nonius Mach3; $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); $T = 193(2)$ K; graphite monochromator; data collection mode ω scans; measurement range: $2.78 \leq \theta \leq 26.27$; section of the reciprocal lattice: $-17 \leq h \leq 0$, $-0 \leq k \leq 17$, $-0 \leq l \leq 26$; of 2441 measured reflections, 2433 were independent, and 1907 with $I > 2\sigma(I)$; linear absorption coefficient 1.183 $\mathrm{mm^{-1}}$; absorption correction ψ scans. The structure was solved by direct methods using SHELXS-86 and refined with all data (298 parameters) by full-matrix least-squares on F^2 using SHELXL93;[5] all non-hydrogen atoms were refined anisotropically; $R_1 = 0.0391$ (observed reflections); $wR_2 = 0.0987$ (all data); max./min residual electron density $0.514/-0.421\ \mathrm{e\,nm^{-3}}$.[5]

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Diastereoselective and Enantioselective Palladium-Catalyzed Allylic Substitution with Nonstabilized Ketone Enolates**

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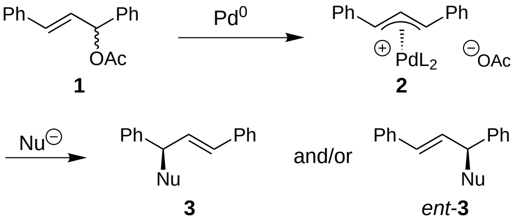
Dedicated to Professor Rolf Huisgen
on the occasion of his 80th birthday

The utility of transition metal mediated allylic substitutions in organic syntheses has been proven by numerous applications in the past three decades. A particularly efficient way of carbon–carbon bond formation was opened up by the reaction of carbon nucleophiles with allylpalladium complexes, the generation of which is accomplished in situ and requires only catalytic amounts of the transition metal.[1] After mechanistic studies had treated the problem of stereochemistry,[2] considerable efforts were directed towards enantioselective variants,[3] most of this work focussed on symmetrically substituted racemic allyl compounds such as **1**. The attack of a nucleophile on the palladium complex **2**, formed from **1**, can be directed in an enantioselective way by means of chiral ligands (L*) so that either one of the substitution products, **3** or *ent*-**3**, can be prepared in a controlled manner [Eq. (1)].[4]



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Despite this impressive progress, the main limitation of this concept is that the carbon nucleophiles used so far have been almost exclusively "soft", stabilized carbanions.[3] Although the chemistry of "preformed" enolates[5] evolved at the same time as that of allylpalladium chemistry, attempts to combine both concepts have been very rare, and their success rather limited. An early report on palladium-catalyzed reactions of ketone enolates with cyclic allyl acetates[6] was questioned later.[7] Furthermore, these attempts were plagued by the inevitable double allylations, low reactivities, and moderate yields.[8a] These difficulties were partly overcome by the employment of enol stannanes instead of lithium enolates,[8] an approach which led to the first enantioselective variant.[9]

Recently, stereoselectivity was obtained in the reaction of an enantiopure allyl acetate with a chelated zinc enolate.[10] However, the problem of producing a palladium-mediated allylation of enolates which provides both diastereoselectivity and catalyst-induced enantioselectivity has so far not been solved. Herein we report, as a solution to this problem, a method that is applicable to cyclic and acyclic ketone enolates.

Two adjacent stereogenic centers are created in the reaction of an α-substituted enolate and the meso complex **2**, which is formed in situ from the racemic acetate **1** [Eq. (1)]. Thus, we decided to tackle the problem of diastereoselectivity first. For this purpose, cyclohexanone was deprotonated with various bases in tetrahydrofuran to generate the enolate **4**; the advantage of this intermediate is its fixed enolate geometry (*E*, Scheme 1). The enolate **4** was allowed to react with the acetate **1** in the presence of 5 mol% of the palladium catalyst generated in situ from tris(dibenzylideneacetone)dipalladium–chloroform ($[Pd_2(dba)_3] \cdot CHCl_3$)[11] and the corresponding phosphane ligands **5**. In all the cases that are listed in Table 1 there was smooth and quantitative conversion into the diastereomeric ketones **6a** and **7a**, which can clearly be distinguished from one another by the chemical shifts of their allylic protons (3.88 and 3.98 ppm, respectively) in the ^1H NMR spectra.

The diastereoselectivity was influenced not only by the ligands **5a–d**[12] on the transition metal but also by the enolate counterion and the base used for the deprotonation. For the lithium enolate, substantial diastereoselectivity resulted from the use of chelating phosphane ligands (Table 1, entries 1

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