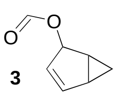

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[13] A Nazarov-type cyclization to **3** would be possible in analogy to **10**, but would be disfavored by strain.

[14] The near degeneracy of the $HOMO_{-1}$ and $HOMO_{-2}$ is a consequence of the weak interaction between the two oxygen lone pairs.

[15] Subjacent orbital control of some forbidden hydrocarbon reactions has been proposed by Berson and Salem.[16] The situation here is somewhat different in that the three HOMOs shown in Figure 3 are essentially noninteracting. Furthermore, the [3,3] and [3,5] rearrangements of **4** are both orbital symmetry allowed.

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[19] These structures were only optimized at the RHF/6-31G** level.

[20] A second-order saddle point with C_s symmetry for this rearrangement has been calculated,[5] but no TS was reported. The three lowest energy conformations of **1** were recalculated (**1a–c** in this work correspond to **5**, **3**, and **1**, respectively, in ref. [5]).

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Canted Ferromagnetism in a Ni^{II} Chain with a Single End-to-End Azido Bridge**

Chang Seop Hong and Youngkyu Do*

With regard to the factors that affect magnetic exchange pathways between paramagnetic centers, the proper choice of bridging ligands is of importance since they influence the magnetic strength and behavior of the molecules. The azido ligand has been widely utilized because its diverse binding modes lead to variations in the magnetic properties that depend on its orientation with respect to the magnetic centers.[1] The structural variety of azido complexes spans from dinuclear,[2] tetranuclear,[3] cubane,[4] one-dimensional,[5] two-dimensional,[6] to three-dimensional compounds.[7] The coordination modes generally observed for the bridging azido group are end-on with ferromagnetic interaction and end-to-end with antiferromagnetic coupling. An example of end-to-end mode for an azido group with ferromagnetic coupling is still lacking, although such systems are favored according to theoretical calculations.[5] Hence, it would be of interest to extend the studies on the magnetic properties of azido compounds by utilizing nonchelating capping ligands, which allow some freedom in the complexation process.[8] We employed the nonchelating capping ligand 3(5)-methylpyrazole to prepare new azido complexes. Here we report the synthesis, structure, and properties of a new one-dimensional compound $[\{Ni(5\text{-methylpyrazole})_4(N_3)\}_n](ClO_4)_n\cdot nH_2O$ (**1**),[9] the first ferromagnetic end-to-end azido complex involving spin canting.

A perspective view of the asymmetric unit and of one symmetry-related fragment of the chain complex **1** is shown in Figure 1. Crystallographic inversion centers are located at the two nickel atoms, which have octahedral coordination environments. The nickel center Ni1 forms relatively uniform bonds to the surrounding nitrogen atoms (Ni1–N11 2.106(3), Ni1–N21 2.105(3), Ni1–N1 2.098(3) Å), while Ni2 has a more distorted geometry owing to a slight equatorial contraction and axial elongation (Ni2–N31 2.097(3), Ni2–N41 2.082(3), Ni2–N3 2.124(3) Å). The equatorial least-squares planes of the two Ni centers are not parallel and form a dihedral angle of 60.6°.

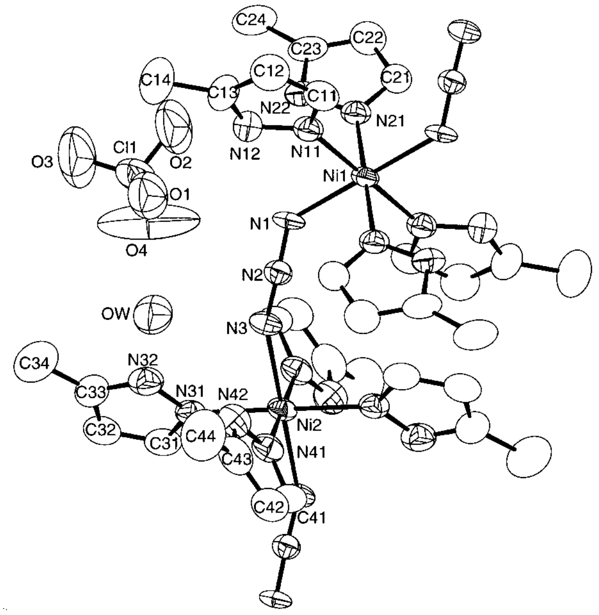

Figure 1. Perspective view of the asymmetric unit of **1** (50% thermal ellipsoids).

The bridging azido ligands link the nickel centers to form one-dimensional chains with a unique end-to-end coordination mode in which two neighboring nickel centers occupy *cis* positions with respect to the azido group. To our knowledge,[5] this is the first example of a μ-azido nickel(II) complex with end-to-end coordination. The Ni1-N_3-Ni2 torsional angle of 75.7° is large for an azido nickel(II) compound.[5] The unique coordination mode and the large torsional angle can be regarded as a manifestation of the structural freedom provided by the nonchelating capping ligands in the complexation process. The two Ni-N-N bond angles of the end-to-end azido group are different (Ni1-N1-N2 128.4(2), Ni2-N3-N2 146.1(3)°). The intrachain distance between the adjacent nickel centers is 5.717 Å, and the shortest interchain distance between nickel centers is 9.815 Å.

The magnetization *M* of **1** was measured in the temperature range 1.8–300 K at 100 G (Figure 2). Upon lowering the

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[*] Prof. Y. Do, C. S. Hong
Department of Chemistry and Center for Molecular Science
Korea Advanced Institute of Science and Technology
Taejon 305-701 (Korea)
Fax: (+82) 42-869-2810
E-mail: ykdo@single.kaist.ac.kr

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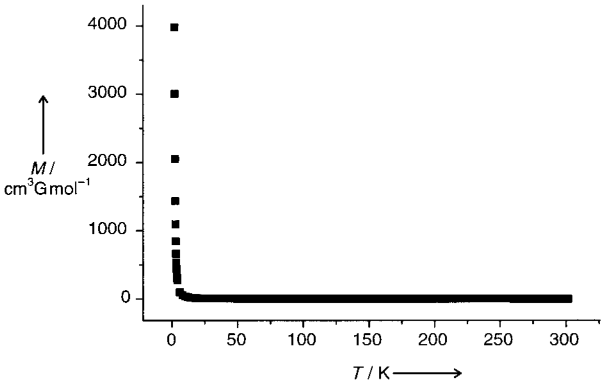

Figure 2. Plot of magnetization M versus temperature T for **1**.

temperature, the M value of 0.432 cm^3 G mol^{-1} at 300 K increases gradually to 98.42 cm^3 G mol^{-1} at 6 K and then rises sharply to 3980 cm^3 G mol^{-1} at 1.8 K, indicative of the onset of a long-range interaction in the lattice. Since the slope dM/dT is still increasing at the experimental temperature limit of 1.8 K; the critical temperature is probably slightly lower than 1.8 K. The magnetic properties of **1** can be interpreted by a Curie–Weiss law [$\chi_m = C/(T-\theta)$] in the temperature range 30–300 K. The best fit leads to $C = 1.244$ cm^3 K mol^{-1} ($g = 2.23$) and $\theta = 11.1$ K. By means of an infinite chain model,[10] the magnetic parameters are estimated to be $g = 2.21$ and $J = 6.91$ cm^{-1}. The positive J value suggests the presence of a ferromagnetic exchange interaction transmitted by the azido group. According to the literature criteria,[5] the expected magnetic phenomenon for **1** would be antiferromagnetic ordering, since the Ni-N-N(azido) bond angles of 128.4(2) and 146.1(3)° deviate from the value of around 164°, at which incidental orthogonality is achieved at a torsion angle of 0°. This apparently conflicts with the experimental observation of ferromagnetic behavior. We attempted to resolve this in terms of the large Ni-N_3-Ni torsional angle of 75.7°, which may minimize the antiferromagnetic contribution and favor a ferromagnetic interaction in chains of **1**.[5, 11]

The magnetization M was measured with variation of the applied magnetic field H from 0 to 70000 G (0–7 T) at 1.8 and 5 K (Figure 3). The experimental saturation value of 1.97 $N\beta$ at 7 T does not reach the value of $gN\beta \approx 2.2\,N\beta$ predicted by the Brillouin equation with $S = 1$ for noninteracting entities in a lattice.[12] This indicates that the spin value of the Ni^{II} ion in the ground state is smaller than $S = 1$, and hence spin canting is operative in **1**. In addition, the abrupt approach of M to the saturation value at 1.8 K is reminiscent of a magnet.

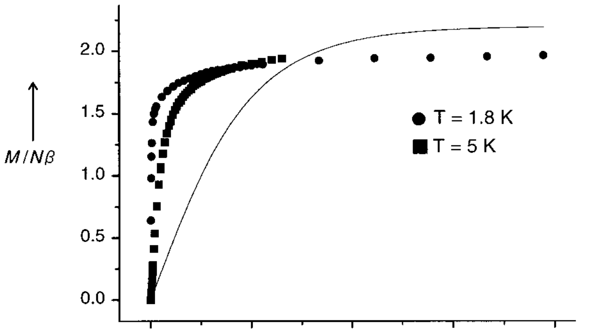

Figure 3. Plot of magnetization isotherms as a function of field strength (H/T) for **1** at 1.8 and 5 K. The solid line represents the Brillouin calculation for $S = 1$.

Given a dihedral angle of 60.6° and a torsional angle of 75.7°, a possible pattern for spin canting can be suggested. Figure 4 illustrates spin canting in which the magnetic spins are coupled ferromagnetically but slightly tilted with respect to each other. This pattern for requires no minimum valley in the $\chi_m T$ curve,[13] as is observed for **1**, and is consistent with the experimental results displayed in Figures 2 and 3.

Figure 4. Schematic drawing of a possible spin canting pattern in **1**.

Experimental Section

1: To an aqueous solution (10 mL) of nickel perchlorate hexahydrate (0.50 mmol) was added neat 3(5)-methylpyrazole (2.0 mmol). After being stirred for 10 min, the resulting solution was treated dropwise with an aqueous solution of sodium azide (10 mL, 0.50 mmol). The pale green solution was filtered and the filtrate was left undisturbed. Well-shaped blue crystals of **1** formed (36% yield). Elemental analysis calcd for $C_{16}H_{26}ClN_{11}NiO_5$: C 35.16, H 4.79, N 28.19; found: C 35.15, H 4.94, N 28.56; IR: $\nu = 2092$ cm^{-1} ($\nu_a(N_3^-)$). The synthesis of the **1** requires not only use of the correct stoichiometry but also slow addition of an aqueous solution of sodium azide to the aqueous reaction mixture of Ni^{II} and 3(5)-methylpyrazole. Otherwise, the mononuclear compound [Ni(5-methylpyrazole)$_4$(N_3)$_2$] is formed.

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[9] X-ray structure analyses: Enraf-Nonius CAD4TSB diffractometer, Mo$_{K\alpha}$ radiation, $\lambda = 0.71071$ Å, Lorentz polarization, $\omega/2\theta$ scans. The structure was solved by direct methods with the SIR92 program and refined anisotropically for non-hydrogen atoms by full-matrix least-squares methods with SHELXS93. All hydrogen atoms were calculated at idealized positions and refined with an overall isotropic factor. Crystal data for **1** ($C_{16}H_{26}ClN_{11}NiO_5$): $M_r = 546.64$, space group $P2_1/n$, $a = 11.434(1)$, $b = 9.815(1)$, $c = 22.576(1)$ Å, $\beta = 102.68(1)°$, $V =$

2471.8(3) Å^3, $Z = 4$, $\rho_{calcd} = 1.469$ g cm^{-3}, $R1 = 0.048$ based on F, $wR2 = 0.133$ based on F^2. Maximum and minimum heights in the final difference Fourier map are 0.578 and -0.378 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101870. 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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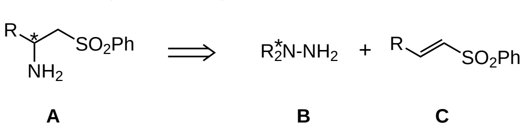
Enantioselective Synthesis of β-Amino Sulfones by aza-Michael Addition to Alkenyl Sulfones[**]

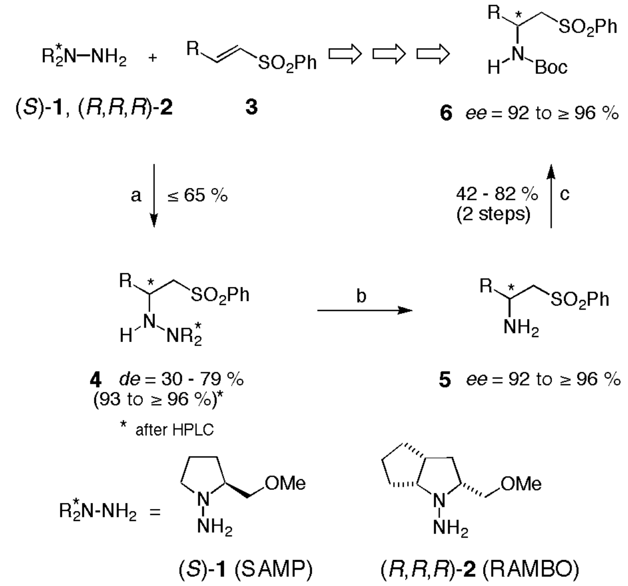
Dieter Enders,[*] Stephan F. Müller, and Gerhard Raabe

Dedicated to Professor Elias J. Corey
on the occasion of his 70th birthday

The use of sulfones in organic synthesis has become increasingly important in recent years. This has been due to versatile synthetic transformations involving sulfones, for example functionalization in the α position by electrophilic substitution, replacement of the sulfone group with other functional groups, and reductive cleavage of the sulfone group. Furthermore, α,β-unsaturated sulfones are excellent Michael acceptors and react with a number of carbon and heteroatom nucleophiles, such as alcohols, thiols, and amines.[1] The aza-Michael addition involving C–N bond formation has proven to be a particularly useful synthetic tool.[2] The conjugate addition of an enantiopure ammonia equivalent **B**, bearing a readily cleaved chiral auxiliary, to alkenyl sulfones **C** should provide a novel enantioselective access to synthetically valuable β-amino sulfones **A**.



Enantiopure β-amino sulfones play an important role in physiological processes.[3] Additionally, they readily undergo electrophilic substitution in the α postion and have, for instance, been used as intermediates in the synthesis of α-amino acids,[4, 5] amino alcohols,[6] substituted uridines and adenosines,[7] alkaloids,[8] β-lactams,[9] and nitrogen heterocycles.[10, 11] As early as the 1960s Stirling and McDowell investigated the kinetics of the intermolecular addition of achiral amines to alkenyl sulfones.[12] Today, there exist several procedures for intramolecular[6, 8, 13] and intermolecular[7, 10, 11, 14] aza-Michael additions to alkenyl sulfones. However, to our knowledge the enantioselective aza-Michael addition with a nitrogen nucleophile bearing chirality information, which may subsequently be cleaved, has not been described. We now report the synthesis of the title compounds by asymmetric conjugate addition with (*S*)-1-amino-2-methoxymethylpyrrolidine (SAMP, (*S*)-**1**)[15] as a chiral ammonia equivalent; this species has already been proven to be of great value in asymmetric synthesis. As shown in Scheme 1, conjugate addition of (*S*)-**1** to (*E*)-alkenyl sulfones (*E*)-**3a**–**e** afforded Michael adducts (*R*,*S*)-**4a**–**e** in the presence of catalytic amounts of ytterbium trifluoromethanesulfonate (Yb(OTf)$_3$)[16] in moderate chemical yields and with moderate to good diastereoselectivities. The epimers could be separated by preparative HPLC to yield virtually diastereomerically pure β-hydrazino sulfones (*R*,*S*)-**4a**–**e** (*de* = 93 to greater than 96 %, Table 1). The absolute configuration of the newly formed stereogenic center of the major diastereomer was determined by X-ray structural analysis of crystalline (*R*,*S*)-**4b** (Figure 1).[17, 18]



Scheme 1. Enantioselective synthesis of β-amino sulfones by aza-Michael addition on alkenyl sulfones. a) 1.5 equiv of nitrogen nucleophile (*S*)-**1** or (*R*,*R*,*R*)-**2** per equiv of sulfone **3**, Yb(OTf)$_3$ (0.1 equiv), THF, room temperature (RT) for 20 d (procedure A) or heating at reflux for 3 d (procedure B); b) BH$_3$ · THF (10.0 equiv, 1N in THF), THF, reflux, 5 h; HCl (4N), RT, 2 h; c) Boc$_2$O (10.0 equiv), Et$_3$N, MeOH, RT, 2 d. OTf = trifluoromethanesulfonate.

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[*] Prof. Dr. D. Enders, Dipl.-Chem. S. F. Müller, Dr. G. Raabe
Institut für Organische Chemie der Technischen Hochschule
Professor-Pirlet-Strasse 1, D-52074 Aachen (Germany)
Fax: (+49) 241-888-8127
E-mail: enders@rwth-aachen.de

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