bond may be due in part to the relativistic contraction of the 6s electron pairs, which are only available for bond formation to a limited extent.[17] Furthermore, this mode of bond formation clearly demonstrates that the lengths of homonuclear double bonds between the heavier elements of Group 14 may well be in the same range as or even larger than the corresponding single bonds.

Experimental Section

At $-110\,^{\circ}C$ solid lead(II) chloride (5.6 g, 20 mmol) was added to a solution of the Grignard reagent TipMgBr, prepared from 1-bromo-2,4,6-triisopropylbenzene (11.44 g, 40.4 mmol) and magnesium (3.0 g, 123 mmol) in THF (100 mL), and the resultant mixture was warmed with vigorous stirring to room temperature within 20 min. The THF solvent was removed by distillation under vacuum, and the residue extracted with *n*-hexane ($2\times$ 50 mL). After separation of the magnesium salts the violet solution was concentrated to a volume of 40 mL and allowed to crystallize at $-50\,^{\circ}C$. Red crystals (5.8 g, 47%) of **4** were obtained: m.p. 75 °C (decomp.). Spectroscopic data of **3** in solution: ^1H NMR (300 MHz, [D$_8$]toluene, 283 K): $\delta = 1.14$ (d, 24H, $^3J(H,H) = 6.7$ Hz), 1.23 (d, 12H, $^3J(H,H) =$ 6.9 Hz, 2.72 (m, 2H), 2.82 (m, 4H), 7.68 (s, 4H); ^{13}C NMR (75 MHz, [D$_8$]toluene, 283 K): $\delta = 24.22$, 24.37, 35.56, 36.28, 128.57, 147.45, 157,45, 255.62 (*ipso*-C, $^1J(^{13}C,^{207}Pb) = 1100$ Hz at 298 K); MS (CI, isobutane): *m/z* (%): 614 (100, M^+); UV/Vis (*n*-hexane): λ_{max} (ε) = 321, 385, 541 nm (960). Elemental analysis of **4** ($C_{60}H_{92}Pb_2$): found (calcd): C 58.57 (58.70), H 7.68 (7.55).

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Keywords: carbene analogues · lead · main group elements · multiple bonds

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[1,3], [3,3], and [3,5] Sigmatropic Rearrangements of Esters Are Pseudopericyclic[**]

David M. Birney,[*] Xiaolian Xu, and Sihyun Ham

In 1969 the famous paper by Woodward and Hoffmann describing the conservation of orbital symmetry was published in this journal.[1] All of the well-known rules regarding pericyclic reactions assume that there is a cyclic loop of interacting π orbitals. However, it is possible to have a pericyclic reaction in which this condition is not fulfilled, that is, in which there is *not* cyclic π overlap. The unique characteristics of these "pseudopericyclic" reactions[2] have been described in detail elsewhere;[3] they can be briefly summarized as follows: 1) These reactions have planar transition states, 2) they may have very low barriers if the

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geometries and the nucleophilic/electrophilic sites are favorable, and 3) no pseudopericyclic reaction can be forbidden by orbital symmetry. Figure 1 shows selected basis orbitals of esters. We recognized that this functional group is capable not only of pericyclic reactions involving the π system, but also of pseudopericyclic reactions involving only the in-plane σ bond and the lone pairs. The results reported here are the first from an ongoing study of concerted reactions of esters.

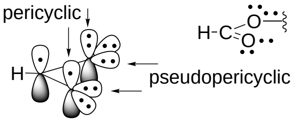
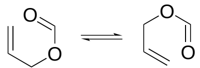


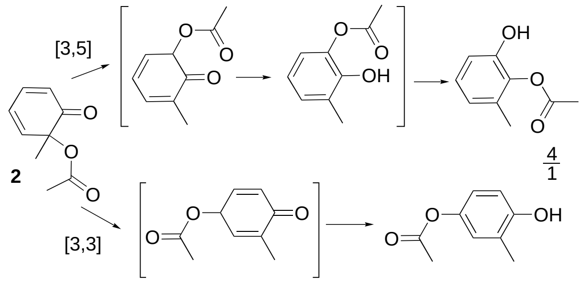
Figure 1. The π, σ, and lone pair basis orbitals of esters. If a reaction involves the π system it is pericyclic, but if the breaking bond and the lone pair do not overlap with the π system, the reaction is pseudopericyclic.

Experimental studies of sigmatropic rearrangements of allyl esters such as **1** [Eq. (1)] indicate a concerted reaction with partial carbonium and carboxylate ion character.[4] Recent ab initio[5] and density functional theory (DFT) calculations[6] found a chair and a flattened boat transition state for this reaction. The chair geometry is similar to that of the Claisen rearrangement.[7] The boat is lower in energy, and the partial bonds are nearly coplanar with the ester group. Zipse recognized that the geometry of this transition state "precludes efficient interaction of the formyl and allyl group π-systems as expected in [3,3]-sigmatropic rearrangements" and describes the reaction as an "intramolecular nucleophilic substitution reaction". He did not generalize from this observation, but we anticipate that a [3,5] sigmatropic rearrangement with a pseudopericyclic geometry is also possible.



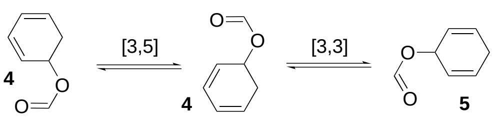
1 **1** (1)

Indeed, in acyloxycyclohexadienones which can undergo both [3,3] and [3,5] sigmatropic rearrangements (e.g. **2**), the major products observed are from formal [3,5] rearrangements (Scheme 1).[8] Tantalizingly, the authors suggested a concerted pathway. In a later review article, this mechanism was discounted; it was *assumed* that "concerted rearrangements of this type are not allowed by orbital symmetries".[9] We undertook the ab initio study presented here with the expectation that the [3,5] sigmatropic rearrangement of esters would in fact be allowed by a pseudopericyclic pathway.[10]



Scheme 1.

The rearrangements of 2,4-cyclohexadienyl formate (**4**, Scheme 2) were chosen as a model system for those in Scheme 1.[13] The geometries of **4** and **5** were calculated, and



Scheme 2.

transition states (TSs) **6** and **7** for a [3,5] and a [3,3] sigmatropic rearrangement of **5** were located (Figure 2). The calculated barrier for the [3,3] rearrangement of **4** to **5** via the boat TS **7** is 38.3 kcal mol^{-1}. If the [3,3] rearrangement is allowed, then the conventional wisdom of the Woodward–Hoffmann rules leads us to expect a much higher barrier for the vinylogous [3,5] process. However, the TS **6** is pseudopericyclic, with the breaking and forming bonds in the plane of the formate (177.0°). And here is the surprise: The barrier calculated for this [3,5] rearrangement via **6** is 3.0 kcal mol^{-1} *lower* in energy than that for the [3,3] rearrangement!

How can this be? Both the [3,3] and the [3,5] rearrangements are in fact orbital symmetry allowed, the latter because it is pseudopericyclic.[3d] These are perhaps most easily understood in terms of the frontier molecular orbital interaction of a formate anion and either an allyl or a cyclohexadiene cation (Figure 3). The three HOMOs of the formate anion are the π_2 orbital and two linear combinations of oxygen lone pairs. The close spacing of these orbitals (0.6 eV) means that any one of them can have a stabilizing interaction with the LUMO of the cation.[14] The π_2 orbital as well as the HOMO$_{-2}$ are of the proper symmetry to interact with the LUMO of the allyl cation, while the HOMO$_{-1}$ can interact with the LUMO of the cyclohexadienyl group.[15]

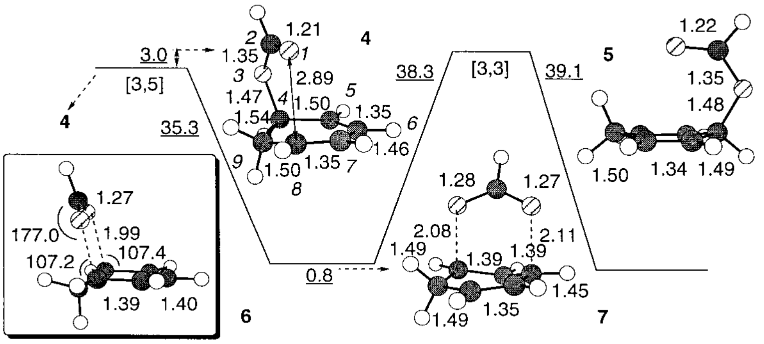


Figure 2. Relative energies (MP4/6-31G** + ZPE, underlined) [kcal mol^{-1}] and MP2/6-31G**-optimized geometries of **4** and **5** and transition states for the [3,5] and [3,3] sigmatropic rearrangement (**6** and **7**). Distances are in Å, angles between planes in degrees. Carbon and oxygen atom numbers are in italics.

The barrier for the [3,3] rearrangement of **4** to **5** might be expected to be lower because this reaction is slightly exothermic (0.8 kcal mol^{-1}), yet it is higher than for the

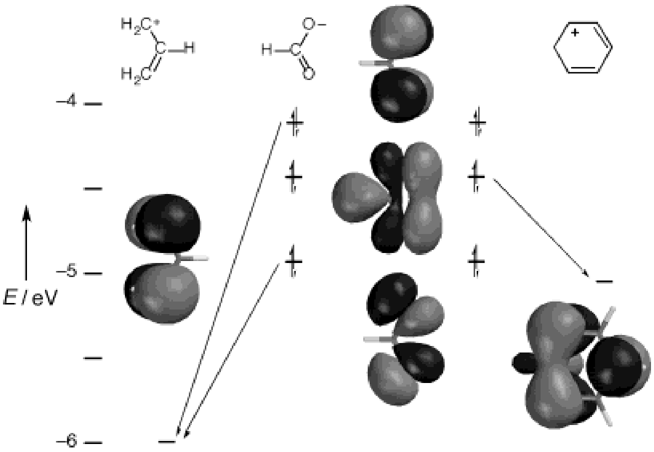
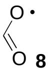


Figure 3. RHF/6-31G** orbitals of allyl cation (LUMO: −6.0 eV; MP2/6-31G** geometry), acetate anion (HOMO: −4.2 eV, HOMO$_{-1}$: −4.4 eV, HOMO$_{-2}$: −4.8 eV; geometry from **6**), and cyclohexadienyl cation (LUMO: −5.0 eV; geometry from **6**).

thermoneutral [3,5] rearrangement. Our experience suggests that the differences in barriers may reflect subtle differences in TS geometries.[3d] Indeed, the [3,3] TS (**7**) is more distorted than the [3,5] TS (**6**). In **6**, the pentadienyl system is essentially planar, while in **7** it is significantly twisted. The facile downward bend of the C9 methylene group in **6** tips the p orbitals of C4 and C8 inwards, towards the ester oxygen atoms, which are closer together (2.31 Å) than these carbon atoms (2.47 Å). Also, in **6** the angle between the plane of the ester and the plane of the pentadienyl fragment is 107.4°, which is similar to the Burgi–Dunnitz trajectory for nucleophilic addition. [17] We conclude that the geometry of TS **6** allows the better (pseudopericyclic) orbital overlap.

Since a radical pathway has been suggested,[9a] we also calculated the energy of separated formyl (**8**) and cyclohexadienyl radicals (**9**; UMP2/6-31G**, admittedly not the best level for calculations of radicals). These are 92.9 kcal mol^{-1} above the energy of TS **6** calculated at the MP2/6-31G** level. Alternatively, an estimate of 77 kcal mol^{-1} for the formation of the radicals may be made from known bond dissociation energies and group additivities. [18] Because the barriers are much lower, it is unlikely the radicals are involved.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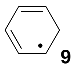
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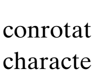
In searching for a [3,5] sigmatropic rearrangement of a formate ester, we also considered the simplest system, the rearrangement of **10**. For this reaction, optimization of a TS constrained to C_s symmetry led not to a [3,5] rearrangement, but to **11**, which is a boat TS for a [3,3] rearrangement of **12** (Figure 4). It is unlikely that **10** directly rearranges to **12** via this C_s-symmetrical TS since the thermal electrocyclic ring closure of the cyclopentadienyl fragment, if cationic, should be conrotatory (C_2). The boat (**11**) exhibits pseudopericyclic character; the angle between the planes of the formate and the partial bonds is 144.0°. This indicates participation of both the π_2 orbital and HOMO$_{-2}$ acetate orbitals.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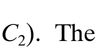
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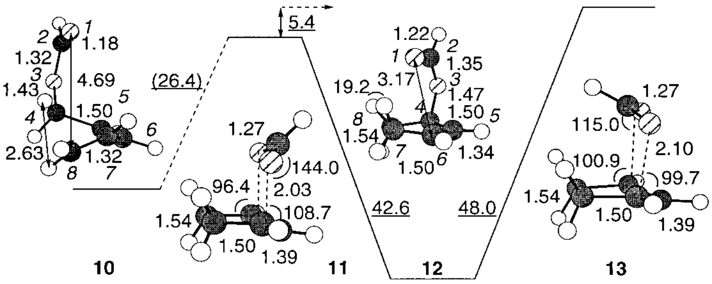
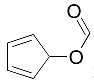


Figure 4. Relative energies (MP4/6-31G**) and MP2/6-31G**-optimized geometries of **11**–**13** as well as relative energy and geometry (RHF/6-31G*) of **10**. See Figure 2 for key.

A chair TS **13** was also located at the RHF/3-21G and MP2/6-31G** levels. Optimization at the RHF/6-31G** level led to the boat (**11**). The chair is 5.4 kcal mol^{-1} higher in energy than the boat and is not pseudopericyclic; the angle between the formate and the partial bonds is only 115.0°. The angles between the partial bonds and the allyl moiety in **11** and **13** are 108.7 and 99.7°, respectively, and are also typical of those found in pericyclic reactions. The chair is apparently destabilized in part by steric crowding between the formate anion and the hydrogen atoms on C7 and C8; the angle between the C4-C6-C7-C8 plane and the partial bonds is 96.4° in **11**, but is opened to 100.9° in **13**.

It appears to us that the inside hydrogen atoms keep the ends of the pentadienyl system too far apart for the formate to bridge them in a [3,5] TS (O1–C8 4.69 Å in **10**). An obvious alternative was to consider the rearrangement of **15**, in which the ends of the pentadienyl system are bonded. However, only [3,3] TSs were found.[19] The chair (**14**) and the boat TSs (**16**) both exhibit pseudopericyclic character, with angles of 141.5° and 150.7°, respectively, between the formate group and the partial bonds (Figure 5). The structures of **14** and **16** clearly show an isolated double bond between C7 and C8 with single bonds to the allyl cation moiety (C4–C8). A [3,5] TS would have given more antiaromatic cation character to the cyclopentadienyl fragment as compared to **14** and **16**. The barriers to this rearrangement to **14** and **16** (60.4 and 59.6 kcal mol^{-1}, respectively) are significantly higher than for **12**, a clear manifestation of the antiaromaticity of the cationic cyclopentadienyl fragment.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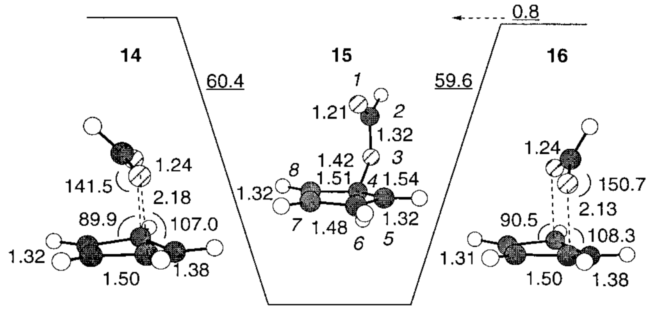
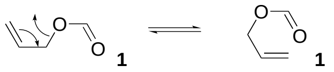


Figure 5. Relative energies and RHF/6-31G**-optimized geometries of **14**–**16**. See Figure 2 for key.

At the suggestion of a referee, we also examined the [1,3] shift of allyl formate [**1**, Eq. (2)]. To the extent that the



1 **1** (2)

breaking C–O bond and the oxygen lone pair are noninteracting, this reaction can also be pseudopericyclic. Alternatively, the HOMO$_{-2}$ of one oxygen atom from the acetate can interact with the LUMO of the allyl cation (Figure 3). The TS for this reaction (**17**) is shown in Figure 6.[20] The barrier of 64.8 kcal mol^{-1} is approximately 20 kcal mol^{-1} above that calculated for the [3,3] rearrangement.[21] Does this mean the reaction is forbidden? No! The strain energy of cyclobutane is estimated to be 24.9 kcal mol^{-1} greater than in cyclohexane.[22] Thus, the higher barrier can be understood to be simply a reflection of the additional strain in the four membered ring transition state for the allowed, pseudopericyclic [1,3] shift of allyl formate.

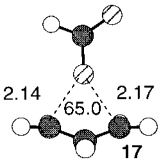


Figure 6. The geometry (MP2/6-31G**) of the transition state **17** for the [1,3] sigmatropic shift of allyl acetate. See Figure 2 for key.

These transition states all show some transfer of charge to the formate moiety, in accord with experiment.[4] The total RHF/6-31G**//MP2/6-31G** Mulliken charges on the formates increase from approximately -0.4 in the ground state molecules to -0.6 in the transition states. There does not seem to be a significant difference between the pericyclic and pseudopericyclic transition states, consistent with both reactions being allowed.

In conclusion, the pseudopericyclic [3,5] sigmatropic rearrangement of **4**, which had been thought to be forbidden, is in fact allowed and is favored by 3.0 kcal mol^{-1} over the [3,3] rearrangement. A [3,5] rearrangement is not found for **10** because the reactive centers are too far apart. The [3,3] rearrangement is also favored in **15** since the cyclopentadienyl cation character of the [3,5] TS would be more antiaromatic. The [1,3] rearrangement of **1** via **17** is allowed, although the four membered ring transition state is strained. The facile [3,5] pseudopericyclic reaction of **4** suggests that whenever there are orthogonal π and/or nonbonding orbitals, the possibility of a pseudopericyclic reaction should be carefully considered.

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[10] The ab initio molecular orbital calculations were carried out with the program Gaussian 94.[11] Transition states showed a single imaginary frequency. The levels of theory used here give qualitatively correct results for allowed pericyclic and pseudopericyclic reactions.[12] The relative energies discussed in the text are from the highest calculated level shown in Table 1. Full geometries and absolute energies are available in the supporting information.

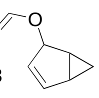
[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**.

[12] a) S. Ham, D. M. Birney, *J. Org. Chem.* **1996**, *61*, 3962–3968; b) D. M. Birney, X. Xu, S. Ham, X. Huang, *J. Org. Chem.* **1997**, *62*, 7114–7120.

Table 1. Calculated relative energies [kcal mol^{-1}], frequency minima $\tilde{\nu}$ [cm^{-1}], zero-point energies (ZPE) [kcal mol^{-1}], and Mulliken charges on the formate group. All calculations were carried out with the 6-31G** basis set and, unless otherwise indicated, at the MP2 level.

	Symmetry	RHF[a,b]	$\tilde{\nu}_{min}$	ZPE	Formate charge[c]	E(MP2)	ΔG(MP2)[d]	E(MP4)[e]
1a	C_s	-0.2	44.2	61.2	-0.40	0.8	0.2	0.4[f]
1b	C_1	0.2	76.7	61.4	-0.40	0.2	0.0	0.1[f]
1c	C_1	0.0	84.7	61.5	-0.40	0.0	0.0	0.0[f]
4	C_1	1.8	72.7	87.6	-0.42	0.1	0.0	0.8
5	C_1	0.0	101.9	87.6	-0.43	0.0	0.0	0.0
6	C_s	39.5	681.5i	86.7	-0.58	30.9	30.5	36.1
7	C_1	40.7	524.0i	86.1	-0.66	36.2	35.3	39.1
8	C_s	–	635.5[a]	13.9[a]	0.0	–		
9	C_{2v}	23.6[g]	178.1[a]	71.8[a]	–	92.9[g]		
10	C_1	15.3	42.9[a]	87.3[a]	-0.40[a]			
11	C_s	41.7	346.5i[a]	86.6[a]	-0.63	39.3		42.6
12	C_1	0.0	109.7[a]	89.1[a]	-0.43	0.0		0.0
13	C_s	–[h]			-0.63	43.2		48.0
14	C_s	60.4	558.7i[a]	70.4[a]	-0.64[a]			
15	C_1	0.0	84.3[a]	72.9[a]	-0.40[a]			
16	C_s	59.6	604.9i[a]	70.6[a]	-0.65[a]			
17	C_1	81.1	467.3i	59.0	-0.65	70.1	67.4	64.8[f]

[a] RHF geometry. [b] With RHF ZPE correction, scaled by 0.9135.[i] [c] Sum of RHF Mulliken charges on the formate group. [d] Relative free energy at 298 K, from unscaled MP2 vibrations. [e] MP4(SDQ,FC) energy, with MP2 ZPE correction, scaled by 0.9646.[i] [f] MP4(SDTQ,FC) energy, with MP2 ZPE correction, scaled by 0.9646.[i] [g] **8** + **9** relative to **5**. [h] The chair form could not located at the RHF/6-31G** level. [i] J. A. Pople, A. P. Scott, M. W. Wong, L. Radom, *Isr. J. Chem.* **1993**, *33*, 345.



3

[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.

[16] a) J. A. Berson, L. Salem, *J. Am. Chem. Soc.* **1972**, *94*, 8917–8918; b) J. A. Berson, R. W. Holder, *J. Am. Chem. Soc.* **1973**, *95*, 2037–2038.

[17] H. B. Burgi, J. D. Dunitz, E. Shefter, *J. Am. Chem. Soc.* **1973**, *95*, 5065–5067.

[18] T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd ed., Harper and Row, New York, **1987**, p. 839.

[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]).

[21] MP4/6-31G** + ZPE.[5]

[22] E. M. Engler, J. D. Andose, P. von R. Schleyer, *J. Am. Chem. Soc.* **1973**, *95*, 8005–8025.

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 $[\{Ni(5\text{-methylpyrazole})_4(N_3)\}_n](ClO_4)_n \cdot n\,H_2O$ (**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°.

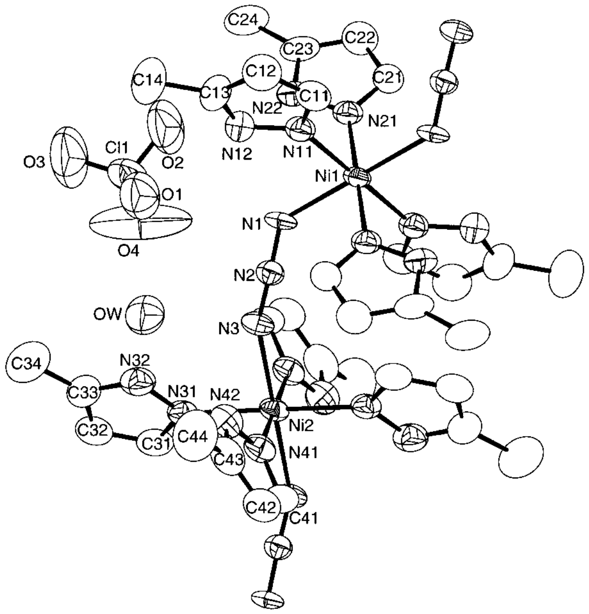


Figure 1. Perspective view of the asymmetric unit of **1** (50% thermal ellipsoids).

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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