

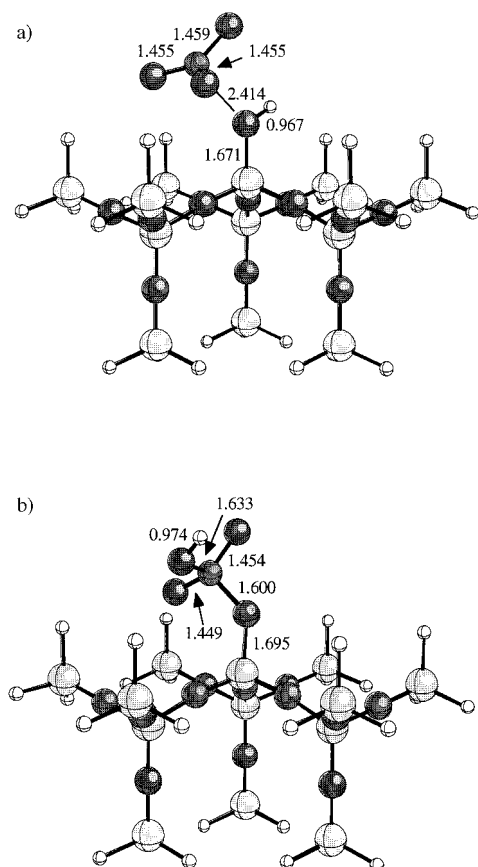


Figure 3. Optimized B3LYP/DZVP2 geometry of the hydrogen sulfate ester formed by reaction of SO_3 on β -cristabolite.

theoretical values compare to experimental deprotonation enthalpies for ZSM-5 of 291–300 kcal mol⁻¹.^[10]

In summary, NMR experiments confirm that adsorption of SO_3 onto oxide surfaces introduces acid sites. On SO_3/ZrO_2 , both Lewis and Brønsted sites are present, and theoretical modeling, in agreement with NMR studies, supports the formation of Brønsted sites on $\text{SO}_3/\text{silica}$.

Experimental Section

Electronic grade silicon(IV) oxide (Puratrem, 99.999 %) was obtained from Strem. This was evacuated at 873 K, cooled to 298 K, and then contacted with SO_3 (0.8 mmol g⁻¹). $\text{SO}_3/\text{silica}$ samples were evacuated at 473 K prior to investigation. Zirconia was prepared by the hydrolysis of zirconyl chloride octahydrate (98 %, Aldrich), followed by washing and drying the gel. All zirconia samples were first calcined at 773 K for two hours in flowing air. SO_3 (1.43 mmol g⁻¹) was adsorbed at 298 K and all samples of $\text{SO}_3/\text{zirconia}$ were further evacuated at 773 K before study. ¹H and ¹⁵N MAS NMR spectra were measured at 9.4 Tesla on a Chemagnetics CMX-360 spectrometer and ¹³C MAS NMR spectra were measured at 4.7 Tesla on a home-built spectrometer.

Theoretical calculations were performed by using Gaussian 94^[11] and the B3LYP^[12] exchange-correlation functional and the DZVP2^[13] basis set. The terminal O and H atoms were held fixed in crystallographic positions, with the OH bond lengths set to 0.9675 Å. Frequency calculations on $\text{H}_3\text{SiOHSO}_3$ and $\text{H}_3\text{SiOSO}_3\text{H}$ were used to estimate the zero-point and thermal energy contributions for the determination of the deprotonation enthalpies of the larger models.

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Syntheses, Structures, and Magnetic Properties of Two Gadolinium(III)–Copper(II) Coordination Polymers by a Hydrothermal Reaction**

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Maochun Hong,* and Wenjian Zhang

Studies on the syntheses, structures, and properties of lanthanide–transition metal complexes are currently of great interest because they are good models to investigate the nature of the magnetic exchange interactions between 3d and 4f metal ions in magnetic materials that contain rare earth metals.^[1–5] Many such studies focused on discrete complexes, which were synthesized from conventional, self-assembly

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reactions in solution.^[1–13] Although several infinite lanthanide–transition metal complexes containing organic ligands have been obtained by conventional solution syntheses,^[14–17] gadolinium(III)–copper(II) polymeric complexes have been poorly explored.^[18] Recently, we tried to use organic ligands to design magnetic complexes that comprise lanthanide and transition metal ions, especially the Gd^{III}–Cu^{II} couple, with infinite structures and we hoped to prepare a useful model of the magnetic exchange in magnetic materials. The key step to form infinite structure architectures is to select appropriate bridging ligands; a rigid, multidentate ligand is helpful. Based on the coordination behaviors of Gd^{III} and Cu^{II}, we chose 2,5-pyridinedicarboxylate (pydc) as the bridging ligand. Unfortunately, the reaction of Gd^{III}, Cu^{II}, and pydc by a conventional solution method, an uncharacterized polymer, insoluble in most common solvents, was obtained. It was apparent that the reaction speed must be reduced to avoid the rapid polymerization and an unusual synthetic method should be employed to obtain single crystals suitable for X-ray analysis. The hydrothermal synthetic method is well known, due to its ability to produce metastable compounds which may not be accessible by the conventional method and thereby promote crystal growth.^[19] After introducing a hydrothermal synthesis, along with using gadolinium oxide and pyridine-2,5-dicarboxylic acid (H₂pydc) as initial reagents, two Gd^{III}–Cu^{II} complexes, $[\{Gd_2Cu_3(pydc)_6(H_2O)_{12}\} \cdot 4H_2O]_n$ (**1**) and $[\{Gd_4Cu_2(pydc)_8(H_2O)_{12}\} \cdot 4H_2O]_n$ (**2**) with infinite structures were isolated and characterized.

The reaction of Gd₂O₃, Cu(OAc)₂, H₂pydc, and H₂O in a molar ratio of 1:2:4:290 at 140°C yielded crystals of **1** suitable for X-ray diffraction analysis. The crystallographic analysis^[20] of **1** revealed that its crystal structure is an one-dimensional (1D) chain polymer. As shown in Figure 1, the chain consists

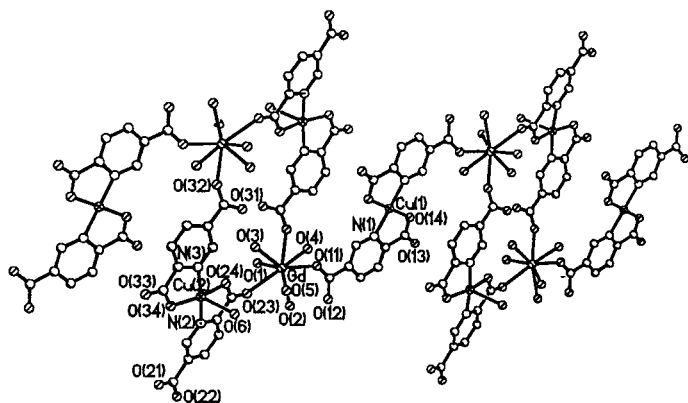
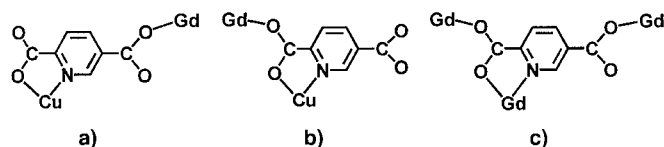


Figure 1. Structure of **1**, showing the 1D organization.

of two building blocks, $[Gd_2Cu_2(pydc)_4(H_2O)_{12}]$ and $[Cu(pydc)_2]$, which are linked to each other by pydc ligands through Gd–O bonds. The chain can also be viewed as two building blocks, $[Cu(pydc)_2]$ and $[Cu(pydc)_2(H_2O)]$, connected by Gd^{III} linkers, in which each Gd^{III} linker connects one $[Cu(pydc)_2]$ and two $[Cu(pydc)_2(H_2O)]$ units. Every Gd^{III} center is coordinated by eight oxygen atoms, three from pydc and five from coordinated water molecules. There are two types of environments for Cu^{II} centers: One in $[Cu(pydc)_2]$ is

chelated by two pydc ligands through its nitrogen and oxygen atoms in an exactly square planar geometry; the other in $[Cu(pydc)_2(H_2O)]$ is surrounded by two nitrogen and two oxygen atoms from the pydc ligands and one oxygen atom from a coordinated water molecule in a square-pyramidal geometry. The coordination modes of the pydc ligands in **1** are shown in Schemes 1 a and b, in which mode b) is seldom found



Scheme 1. Coordination modes of the pydc ligand.

in multicarboxylate ligands, especially in the lanthanide systems. The 1D chains are linked by the hydrogen bonds to form layer structures which are further linked by hydrogen bonds to form the three-dimensional (3D) structure. The Gd–O bond lengths range over 2.329–2.490 Å, while the Cu–O and Cu–N distances in the square plane range over 1.951–1.973 and 1.931–1.966 Å, respectively. The Cu–O_{water} distance (2.381 Å) is rather long, indicating the Cu–O_{water} bond is weak. Gadolinium–gadolinium, gadolinium–copper, and copper–copper distances between the adjacent units are 6.290, 5.801, and 5.119 Å, respectively, indicating a lack of directed M–M interactions.

In an attempt to prepare similar polymers with different Gd:Cu ratios, the reactions of Gd₂O₃, Cu(OAc)₂, H₂pydc, and H₂O at different Gd:Cu:H₂pydc molar ratios were carried out, however, polymer **1** was always obtained. Through the replacement of Cu(OAc)₂ by CuO, we succeeded in the isolation of **2** in high yield. The reaction of Gd₂O₃, CuO, H₂pydc, and H₂O in a molar ratio of 1:2:4:290 at 140°C yielded blue crystals of **2** suitable for X-ray analysis. The structure^[20] of **2** is a 3D polymer, which consists of $[Gd_4Cu_2(pydc)_8(H_2O)_{12}]$ units. Through Gd–O_{pydc} bonds, the units are linked head-to-tail to form infinite zigzag chains (Figure 2), where two neighboring chains are linked to generate wave-like, two-dimensional (2D) structures which are again connected to each other by pydc ligands to produce the 3D structure, as shown in Figure 3. The 2D wave can also be

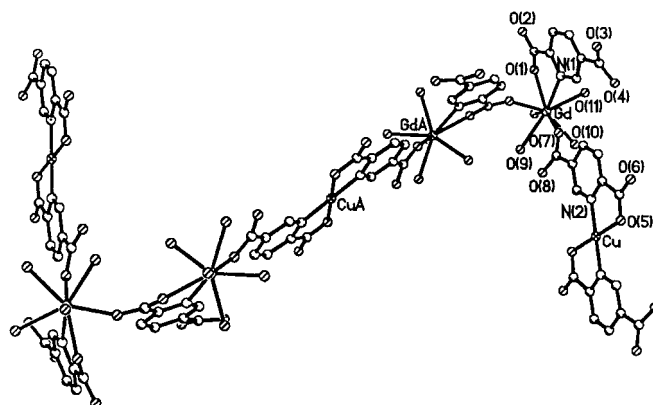


Figure 2. Wavelike structure of **2**; for clarity, only one zigzag chain is shown.

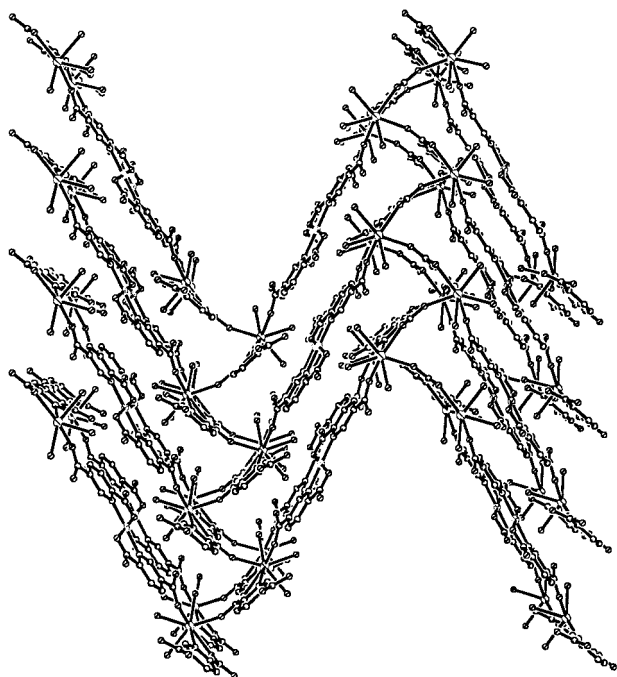


Figure 3. Structure of **2**, showing the packing along the *a* axis.

viewed as Gd–Cu ladders, in which the rungs are formed by [Cu(pydc)₂] species and the sidepieces by Gd^{III} chains; the sidepieces of the neighboring ladders are linked by pydc ligands through Gd–O bonds to yield the wave. Each Gd^{III} center is coordinated by one nitrogen and four oxygen atoms from four pydc ligands and three oxygen atoms from coordinated water molecules. Each Cu^{II} atom is chelated by two pydc ligands through its nitrogen and oxygen atoms in an exactly square planar geometry. The coordination modes of pydc ligands in **2** are also given in Schemes 1a and c. The Gd–O bonds range over 2.338–2.434 Å, while the Gd–N bond is 2.575 Å. The Cu–N and Cu–O bonds are 1.970 and 1.946 Å, similar to those in **1**. Gadolinium–gadolinium, gadolinium–copper, and copper–copper distances between the adjacent units are 6.399, 6.081, and 7.779 Å, respectively.

Interestingly, although the molar ratio of the reagents and the reaction conditions for the syntheses of **1** and **2** are the same, the ratios of Cu/Gd, the structures, the coordination environments of metal centers, and coordination modes of pydc ligands in the two compounds are quite different. For **1**, free Cu^{II} ions are used as reagent (in reaction with Gd₂O₃) and these readily coordinate to the nitrogen atoms of pydc ligands; thus all nitrogen atoms are coordinated by Cu^{II} giving rise to a high Cu/Gd ratio of 3/2. For **2**, the reaction rate of CuO may be comparable with that of Gd₂O₃, thus the nitrogen atoms of pydc are bound simultaneously by Gd^{III} and Cu^{II}, and a low Cu/Gd ratio of 1/2 is obtained. This result may provide a new way to adjust the metal:metal ratio and to control the coordination mode of organic ligands in the lanthanide–transition metal reaction systems which are useful for the designing of model complexes for magnetic materials.

The $\chi_M T$ versus *T* plots of temperature-dependent magnetic susceptibility data for **1** and **2** are shown in Figure 4. For **1**, the value of $\chi_M T$ is 16.44 cm³ K mol^{−1} at 300 K and remains essentially constant to 50 K. It increases slightly below 50 K and reaches its maximum value of 16.87 cm³ K mol^{−1} around

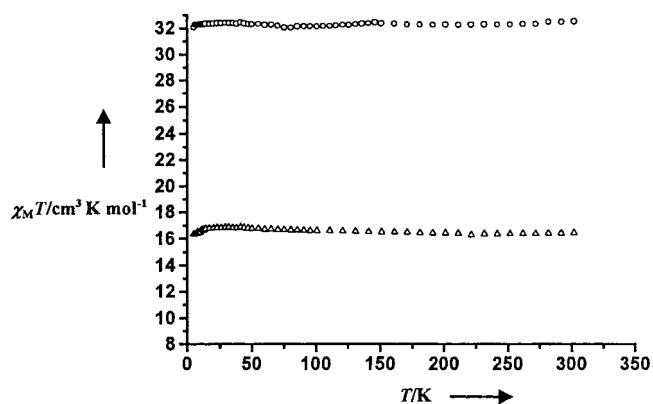


Figure 4. Experimental $\chi_M T$ versus *T* curves for complexes **1** and **2**.

10.7 K, then decreases as *T* is lowered further. For **2**, the values of $\chi_M T$ are essentially constant from 300 to 5 K (the average value is 32.33(20) cm³ K mol^{−1}). The $\chi_M T$ values of **1** at high temperature (*T* > 50 K) and **2** are compared with the calculated values using the Equation (1), which is based on the free-ion approximation for Gd^{III} and Cu^{II}, where *N_A*, β, and *k* are the Avogadro number, the Bohr magneton, and the Boltzmann constant, respectively.

$$\chi_M T = \frac{N_A \beta^2}{3k} \{ \sum g_{\text{Gd}^{\text{III}}}^2 (S_{\text{Gd}^{\text{III}}} (S_{\text{Gd}^{\text{III}}} + 1)) + \sum g_{\text{Cu}^{\text{II}}}^2 (S_{\text{Cu}^{\text{II}}} (S_{\text{Cu}^{\text{II}}} + 1)) \} \quad (1)$$

The magnetic behaviors for **1** and **2** are different from those of discrete gadolinium–copper complexes which normally show ferromagnetic interactions.^[4–9] Detailed studies on magnetic properties and the other polymeric lanthanide–transition metal complexes are underway and will be reported later in a full paper.

Experimental Section

Synthesis of 1: A mixture of Gd₂O₃ (0.090 g, 0.25 mmol), Cu(OAc)₂ (0.100 g, 0.5 mmol), 2,5-pyridinedicarboxylic acid (0.167 g, 1.0 mmol), and H₂O (14.0 mL) in a mole ratio of about 1:2:4:290 was heated in a 25-mL stainless-steel reactor with a Teflon liner at 140°C for 72 h. Green-blue crystals of **1** formed. Yield 20%. Elemental analysis for C₄₂H₅₀N₆O₄₀·Cu₃Gd₂ (%) calcd: C 28.28, H 2.82, N 4.71; found: C 28.54, H 2.80, N 4.74; IR (KBr pellet): $\tilde{\nu}$ = 3385(br, vs), 1612(vs), 1391(s), 1358(s), 1284(m), 1038(m), 768(s), 517(m) cm^{−1}.

Synthesis of 2: An analogous procedure was followed to prepare **2** except Cu(OAc)₂ was replaced by CuO. A mixture of Gd₂O₃ (0.090 g, 0.25 mmol), CuO (0.040 g, 0.50 mmol), 2,5-pyridinedicarboxylic acid (0.168 g, 1.0 mmol), and H₂O (14.0 mL) in a mole ratio of about 1:2:4:290 was heated in a 25-mL stainless-steel reactor with Teflon liner at 140°C for 72 h. Blue crystals of **2** formed. Yield 75%. Elemental analysis for C₃₆H₅₆N₈O₄₈·Cu₂Gd₄ (%) calcd: C 28.44, H 2.39, N 4.74; found: C 29.14, H 2.47, N 4.95; IR (KBr pellet): $\tilde{\nu}$ = 3385(br, vs), 1610(vs), 1392(s), 1358(s), 1286(m), 1038(m), 766(s), 513(m) cm^{−1}.

The magnetic susceptibility data were collected from polycrystalline samples at an external field of 1 kG on a PPMS Model 6000 magnetometer

(Quantum Design) in the temperature range 5 to 300 K. The output data were corrected for the diamagnetism of the sample holder and of the samples, calculated from their Pascal's constants.

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Experimental Observation of Pentaatomic Tetracoordinate Planar Si- and Ge-Containing Molecules: MAI_4^- and MAI_4^{*}

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The chemistry of silicon and germanium is dominated by their tendency to form tetracoordinate tetrahedral structures, just as their more famous congener, the tetracoordinate tetrahedral carbon atom. The tetrahedral carbon idea, proposed by van't Hoff and Le Bel 125 years ago, has been the most important stereochemistry concept in understanding organic and biomolecules. The tetracoordinate tetrahedral structure of C, Si, and Ge atoms is rationalized elegantly by the concept of sp^3 hybridization. However, in the last 30 years chemists have attempted to make unusual compounds that contain *planar* tetracoordinate C, Si, and Ge atoms. In particular, substantial efforts and progress have been made in the design and synthesis of tetracoordinate planar carbon molecules by overcoming the inherent preference for tetrahedral bonding.^[1–6] Tetracoordinate planar silicon molecules have also been studied theoretically^[7] and experimentally.^[8]

We are interested in the generation of planar carbon, silicon, germanium, tin, and lead species in the gas phase and the investigation of their electronic structure and chemical bonding by using a combined experimental and theoretical approach. We recently reported the first observation of a *pentaatomic* tetracoordinate planar carbon molecule (CAI_4^-) which has a planar structure and represents the smallest species to contain a tetracoordinate planar carbon.^[9] Interestingly, however, its neutral CAI_4 parent molecule is tetrahedral. We showed that planarity in CAI_4^- is achieved through ligand–ligand bonding interactions in its HOMO. We also found a general rule, that to achieve planarity in pentaatomic species composed of a first-row central atom and second- or

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- [20] Crystal data for **1**: Crystal dimensions $0.12 \times 0.12 \times 0.08$ mm, $\text{C}_{42}\text{H}_{50}\text{N}_6\text{O}_{40}\text{Cu}_3\text{Gd}_2$, $M_w = 1784.0$, triclinic, space group $P\bar{1}$, $a = 7.393(2)$, $b = 13.576(6)$, $c = 15.169(4)$ Å, $\alpha = 72.62(2)$, $\beta = 76.15(2)$, $\gamma = 80.17(3)^\circ$, $V = 1401.7(7)$ Å³, $Z = 1$, $R(wR) = 0.043(0.097)$ for 4906 reflections with $F \geq 2.0\sigma(F_o)$. Crystal data for **2**: Crystal dimensions $0.45 \times 0.20 \times 0.15$ mm, $\text{C}_{56}\text{H}_{56}\text{N}_8\text{O}_{48}\text{Cu}_2\text{Gd}_4$, $M_w = 2365.2$, monoclinic, space group $P2_1/c$, $a = 9.260(2)$, $b = 25.543(5)$, $c = 7.782(1)$ Å, $\beta = 97.36(2)^\circ$, $V = 1825.3(6)$ Å³, $Z = 1$, $R(wR) = 0.034(0.088)$ for 3179 reflections with $F \geq 2.0\sigma(F_o)$. The intensity data were collected on a Bruker CCD diffractometer with graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) radiation at room temperature. The structures were solved by directed methods and all of the calculations were performed by using the SHELXTL-93 program package on a Legand computer. 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-138940 for **1** and -138941 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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