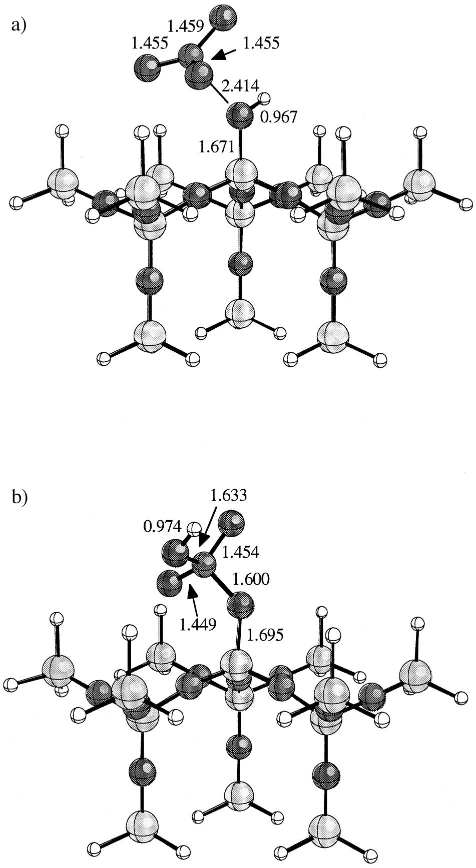

Figure 3. Optimized B3LYP/DZVP2 geometry of the hydrogen sulfate ester formed by reaction of SO_3 on β-cristabolite.

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 SO_3/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}). SO_3/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 SO_3/zirconia were further evacuated at 773 K before study. ^1H and ^{15}N MAS NMR spectra were measured at 9.4 Tesla on a Chemagnetics CMX-360 spectrometer and ^{13}C 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 $H_3SiOHSO_3$ and H_3SiOSO_3H were used to estimate the zero-point and thermal energy contributions for the determination of the deprotonation enthalpies of the larger models.

Received: September 27, 1999
Revised: May 29, 2000 [Z14070]

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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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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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[**] This work is supported by the NNSF of China, the NSF of Fujian Province, and the Key Project from the CAS.

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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 pyidine-2,5-dicarboxylic acid (H_2pydc) 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 Gd_2O_3, $Cu(OAc)_2$, H_2pydc, and H_2O 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 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 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.

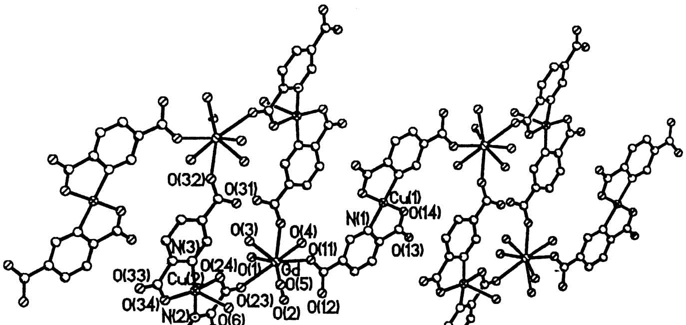
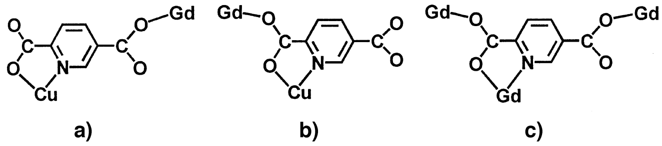


Figure 1. Structure of **1**, showing the 1D organization.



Scheme 1. Coordination modes of the pydc ligand.

In an attempt to prepare similar polymers with different Gd:Cu ratios, the reactions of Gd_2O_3, $Cu(OAc)_2$, H_2pydc, and H_2O at different Gd:Cu:H_2pydc 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 Gd_2O_3, CuO, H_2pydc, and H_2O 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 wavelike, 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

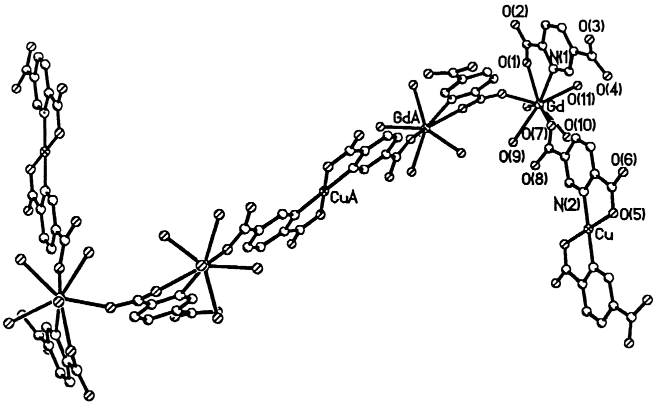


Figure 2. Wavelike structure of **2**; for clarity, only one zigzag chain is shown.

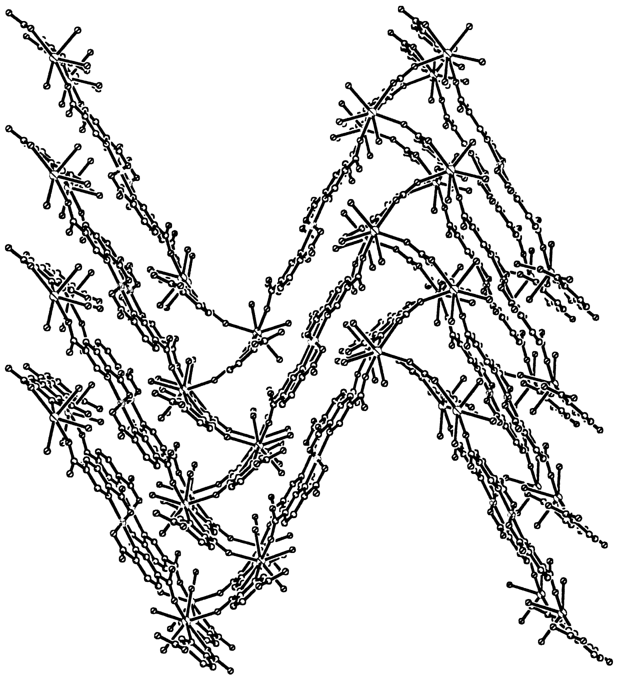


Figure 3. Structure of **2**, showing the packing along the *a* axis.

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 1 a 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 Gd_2O_3) 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 comparible with that of Gd_2O_3, 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 cm^3 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 cm^3 K mol^{-1} around 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) cm^3 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.

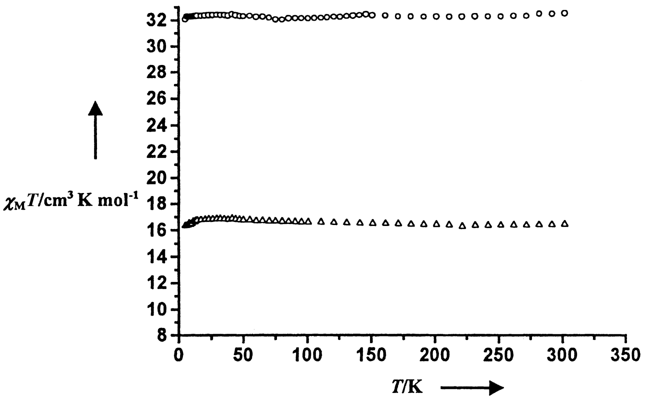


Figure 4. Experimental $\chi_M T$ versus T curves for complexes **1** and **2**.

$$\chi_M T = \frac{N_A \beta^2}{3k}\{\Sigma g^2_{Gd^{III}}(S_{Gd^{III}}(S_{Gd^{III}}+1)) + \Sigma g^2_{Cu^{II}}(S_{Cu^{II}}(S_{Cu^{II}}+1))\} \qquad (1)$$

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 Gd_2O_3 (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 H_2O (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 $C_{42}H_{50}N_6O_{40}Cu_3Gd_2$ (%) 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 prepared **2** except $Cu(OAc)_2$ was replaced by CuO. A mixture of Gd_2O_3 (0.090 g, 0.25 mmol), CuO (0.040 g, 0.50 mmol), 2,5-pyridinedicarboxylic acid (0.168 g, 1.0 mmol), and H_2O (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 $C_{56}H_{56}N_8O_{48}Cu_2Gd_4$ (%) 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.

Received: January 26, 2000
Revised: June 6, 2000 [Z14603]

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[20] Crystal data for **1**: Crystal dimensions $0.12 \times 0.12 \times 0.08$ mm, $C_{42}H_{50}N_6O_{40}Cu_3Gd_2$, $M_w = 1784.0$, triclinic, space group $P\bar{1}$, $a = 7.393(2)$, $b = 13.576(6)$, $c = 15.169(4)$ Å, $\alpha = 72.62(2)$, $\beta = 76.15(2)$, $\gamma = 80.17(3)^\circ$, $V = 1401.7(7)$ Å^3, $Z = 1$, $R(wR) = 0.043(0.097)$ 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, $C_{56}H_{56}N_8O_{48}Cu_2Gd_4$, $M_w = 2365.2$, monoclinic, space group $P2_1/c$, $a = 9.260(2)$, $b = 25.543(5)$, $c = 7.782(1)$ Å, $\beta = 97.36(2)^\circ$, $V = 1825.3(6)$ Å^3, $Z = 1$, $R(wR) = 0.034(0.088)$ for 3179 reflections with $F \geq 2.0\sigma(F_o)$. The intensity data were collected on a Bruker CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ 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 CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Experimental Observation of Pentaatomic Tetracoordinate Planar Si- and Ge-Containing Molecules: MAl_4^- and MAl_4**

Alexander I. Boldyrev,* Xi Li, and Lai-Sheng Wang*

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 genertion 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 (CAl_4^-) which has a planar structure and represents the smallest species to contain a tetracoordinate planar carbon.[9] Interestingly, however, its neutral CAl_4 parent molecule is tetrahedral. We showed that planarity in CAl_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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[**] The theoretical work was done at Utah State University and supported by the donors of The Petroleum Research Fund (ACS-PRF no. 35255-AC6), administered by the American Chemical Society. The experimental work was supported by the National Science Foundation (DMR-9622733) and was performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle Memorial Institute. L.S.W. is an Alfred P. Sloan Foundation Research Fellow.
M = Si, Ge.