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Cyclic and Linear Structures Constructed by Ionic Bonds between Alkali Ion and Pinwheel Pentanuclear $[Gd^{III}(Cu^{II}L)_4]$ Core of $M[Gd^{III}(Cu^{II}L)_4]$ ($M^+ = Na^+$, K^+, and Cs^+; H_3L = *N*-(4-Methyl-6-oxo-3-azahept-4-enyl)oxamic Acid)

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Three copper(II)–gadolinium(III) complexes $M[Gd(CuL)_4]$ with $M^+ = Na^+$, K^+, and Cs^+ have been synthesized, where H_3L denotes *N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid. The anionic part $[Gd(CuL)_4]^-$ assumes a pinwheel-like pentanuclear $GdCu_4$ core and the central Gd^{III} ion is coordinated by eight oxygen atoms of four "(CuL)," where each "(CuL)" assumes a square-planar N_2O_2 coordination geometry and functions as a bidentate chelate ligand to Gd^{III} ion. The sodium and potassium salts assume a one-dimensional (1D) chain structure bridged by Na^+ or K^+ ions, while the cesium salt assumes a cyclic dimeric structure bridged by Cs^+ ions. For the assembly structures, the cation acts as a connector between adjacent $[Ln(CuL)_4]^-$ cores. The magnetic data demonstrated an intracluster ferromagnetic interaction between Gd^{III} and Cu^{II} ions within a $GdCu_4$ core and an intercluster antiferromagnetic interaction through the cation. The magnetic susceptibilities can be reproduced by the spin Hamiltonian based on the pentanuclear $GdCu_4$ structure, $\hat{H} = \beta H(4g_{Cu}S_{Cu} + g_{Gd}S_{Gd}) - 2JS_{Gd}(S_{Cu1} + S_{Cu2} + S_{Cu3} + S_{Cu4})$. The best-fit parameters are $g_{Gd} = 2.00$, $g_{Cu} = 2.12$, $J_{Gd\text{–}Cu} = +1.11\,cm^{-1}$, $zJ' = -0.065\,cm^{-1}$, and 0.4% of monomeric Cu^{II} impurity for the Na^+ salt,; $g_{Gd} = 2.00$, $g_{Cu} = 2.13$, $J_{Gd\text{–}Cu} = +1.03\,cm^{-1}$, $zJ' = -0.038\,cm^{-1}$, and 0.2% of monomeric Cu^{II} impurity for the K^+ salt,; and $g_{Gd} = 2.00$, $g_{Cu} = 2.14$, $J_{Gd\text{–}Cu} = +0.67\,cm^{-1}$, $zJ' = -0.025\,cm^{-1}$, 0.2% of monomeric Cu^{II} impurity for the Cs^+ salt. The Gd–Cu coupling constant J is very similar in the Na^+ and K^+ salts ($+1.11$ and $+1.03\,cm^{-1}$) but is slightly smaller for the Cs^+ salt ($+0.67\,cm^{-1}$), probably due to the different packing of the $GdCu_4$ clusters in the latter salt (cyclic dimers instead of an infinite chain); (2) the intercluster antiferromagnetic interaction, responsible for the low temperature decrease of $\chi_M T$, significantly decreases when the ionic radius of the alkali cation increases ($Na^+ < K^+ < Cs^+$) thus keeping the pentanuclear units further apart.

Self-organization of a simple molecule into supramolecular assembly has allowed the structural versatility and the rational design of functional materials, in which the pre-organized molecule has the programmed information to lead to the supramolecular structure and specific function.[1–3] A variety of bonds from strong to weak in magnitude, such as ionic, covalent, coordination, hydrogen, and π–π bonds can be used for the motive force of the assembly reactions.

Molecular-based magnets have been prepared by the assembly of well-designed components.[4] The discovery of single molecule magnets (SMMs) in Mn_{12} clusters and the subsequent extensive developments are considered to be one of the most important achievements of molecular magnetism.[5] In the molecular design of SMMs, 3d–4f molecular system have attracted much attention,[6] because the high-spin state and the molecular magnetic anisotropy can be easily generated. The recent results with 3d–4f molecular systems on SMMs demonstrate a high possibility of 3d–4f molecular systems for the development of the functional materials.

We look for the p–d–f molecular systems, in which three different elements play roles for the construction of structure or/and function. In this study, we have synthesized copper(II)–gadolinium(III) complexes $M[Gd^{III}(Cu^{II}L)_4]$ ($M^+ = Na^+$, K^+, and Cs^+; H_3L = *N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid) as a p–d–f molecular system. Although these complexes do not satisfy the conditions for SMMs due to the magnetically isotropic components of Cu^{2+} and Gd^{3+}, they have 1D chain and cyclic cluster structures controlled by the size of the cation, in which the cation plays a role of connector between adjacent $[Gd^{III}(Cu^{II}L)_4]^-$ cores. The sodium and potassium salts take a 1D chain structure bridged by Na^+ or K^+ ion, while the cesium salt takes a cyclic cluster structure bridged by Cs^+ ion. We report here the syntheses, structures, and magnetic properties. The Na^+ salt has been partially reported.[7]

Results and Discussion

Synthesis and Characterization of $M[Gd(CuL)_4]$ ($M^+ =$ Na^+, K^+, and Cs^+). The sodium salt of ligand-complex,

Table 1. X-ray Crystallographic Data for $Na[Gd(CuL)_4]\cdot 2MeOH\cdot H_2O$, $K[Gd(CuL)_4]\cdot 3MeOH\cdot H_2O$, and $Cs[Gd(CuL)_4]\cdot 5H_2O$

Complex	$Na[Gd(CuL)_4]$	$K[Gd(CuL)_4]$	$Cs[Gd(CuL)_4]$
Formula	$C_{38}H_{54}N_8O_{19}NaCu_4Gd$	$C_{40}H_{56}N_8O_{20}KCu_4Gd$	$C_{36}H_{44}N_8O_{21}CsCu_4Gd$
FW	1361.3	1419.46	1469.12
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a/Å	14.035(3)	13.997(4)	13.215(5)
b/Å	14.766(3)	14.679(5)	13.489(5)
c/Å	26.088(6)	26.321(7)	16.275(5)
$\alpha/°$			88.645(12)
$\beta/°$	94.590(10)	95.687(9)	70.278(11)
$\gamma/°$			77.299(14)
V/Å^3	5389.1(20)	5381.2(27)	2660.1(15)
Z	4	4	2
$D_{\mathrm{calcd}}/\mathrm{g\,cm^{-3}}$	1.678	1.752	1.834
$\mu/\mathrm{cm^{-1}}$	28.521	29.302	35.583
$R_1{}^{a)}[I > 2.0\sigma(I)]$	0.0586	0.0842	0.0848
$wR_2{}^{b)}$[all data]	0.1735	0.1762	0.2319
T/K	296.1	296.1	296.1

Data with a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

$Na[CuL]\cdot 1.33H_2O$ (H_3L = N-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid), used in this study, was first prepared by Costes et al. and employed in the synthesis of polynuclear copper(II) complexes.[8] The potassium and cesium salts, $K[CuL]\cdot 2.5H_2O$ and $Cs[CuL]\cdot 1.33H_2O$, were prepared according to a similar method to that of the sodium salt. The present series of copper(II)–gadolinium(III) complexes $M[Gd(CuL)_4]$ with $M^+ = Na^+$, K^+, and Cs^+ were prepared by mixing two solutions of $M[CuL]\cdot nH_2O$ ($M^+ = Na^+$, K^+, and Cs^+) and $[Gd(hfa)_3(H_2O)_2]$ (hfa: hexafluoroacetylacetonato) in 4:1 molar ratio in methanol at ambient temperature. Purple colored rhombic crystals of the sodium and potassium salts and needle crystals of the cesium salt suitable for X-ray diffraction analyses were obtained by diffusion, in which a methanolic solution of $[Gd(hfa)_3(H_2O)_2]$ was diffused to a methanolic solution of $M[CuL]\cdot nH_2O$ ($M^+ = Na^+$, K^+, and Cs^+) at ambient temperature. All complexes crystallized as solvates and the crystals lose the crystal solvents even at room temperature to lose crystallinity. A crystal selected was encapsulated in a glass capillary and subjected to X-ray diffraction analysis. After the samples were left in the open atmosphere, other physical measurements such as elemental analyses and magnetic measurements were carried out. The elemental analyses of the sodium salt thus obtained agreed with the formula of non-solvate $Na[Gd(CuL)_4]$, those of the potassium salt agreed with the formula of the trihydrate $K[Gd(CuL)_4]\cdot 3H_2O$, and those of the cesium salt gave a good agreement with the calculated values of the hexahydrate $Cs[Ln(CuL)_4]\cdot 6H_2O$, respectively. The thermogravimetric analyses (TGA) of the potassium and cesium salts showed weight loss corresponding to three and six water molecules, respectively. The magnetic data were calculated on the basis of the formulas given by the elemental analyses.

Structural Descriptions of $Na[Gd(CuL)_4]$ and $K[Gd(CuL)_4]$. The crystal structures of $Na[Gd(CuL)_4]$, $K[Gd(CuL)_4]$, and $Cs[Gd(CuL)_4]$ were determined by single-crystal X-ray diffraction analyses. Table 1 gives the crystallographic data of $Na[Gd(CuL)_4]$, $K[Gd(CuL)_4]$, and $Cs[Gd(CuL)_4]$. Relevant bond distances and angles for three complexes are given in Table 2. As evidenced by the crystallographic data, the sodium and potassium salts are isomorphous to each other, but not to the cesium salt. Figure 1a shows a pentanuclear pinwheel-like $GdCu_4$ core as the anionic part of $Na[Gd(CuL)_4]$ with the selected atom numbering scheme, where the central Gd^{III} ion is coordinated by eight oxygen atoms of four ligand-complexes $(CuL)^-$. The eight Gd–O distances are Gd–O(1) = 2.408(5), Gd–O(2) = 2.413(5), Gd–O(5) = 2.362(5), Gd–O(6) = 2.436(4), Gd–O(9) = 2.366(6), Gd–O(10) = 2.426(5), Gd–O(13) = 2.406(5), and Gd–O(14) = 2.422(5) Å. Each Cu^{II} complex assumes a square-planar N_2O_2 coordination geometry and coordinates to Gd^{III} ion by two oxygen atoms at the terminal oximate site as an electrically mononegative chelate ligand $(CuL)^-$. A similar pinwheel $GdCu_4$ core has been reported by Lloret et al., in which N,N'-bis(3-aminopropyl)-oximatocopper(II) functions as a bidentate *complex-ligand* to Gd(III) ion.[9]

Figure 1b shows the bridging mode around Na^+ ion of $Na[Gd(CuL)_4]$, where a Na^+ ion is coordinated by two oxygen atoms of two oximate groups of two (CuL) in *trans*-position and by those of the adjacent $[Gd(CuL)_4]$ core, with the distances of Na–O(2) = 2.471(6), Na–O(10) = 2.422(6), Na–O(6)* = 2.406(6), and Na–O(14)* = 2.449(5) Å. Figure 2 shows a 1D structure of $Na[Gd(CuL)_4]$ running along the b axis, where Na^+ ion acts as a connector between two adjacent molecules $[Gd(CuL)_4]$ to form a 1D structure with Gd–Gd distance of 7.493 Å and Na–Gd distances of 3.798 and 3.788 Å. Within the 1D chain, a Na^+ ion is bound by two oxygen atoms of two (CuL) of a $[Gd(CuL)_4]$ core and two oxygen atoms of two $(CuL)^-$ of the adjustment core. Further, the Na^+ ion is bound by a water molecule with Na^+–O(19) = 2.400(10) Å. Totally the coordination number of the Na^+ is five.

The crystal structure of $K[Gd(CuL)_4]$ is isomorphous to that of the sodium salt and assumes a similar 1D structure to $Na[Gd(CuL)_4]$, where K^+ ion acts as a connector with the six

Table 2. Relevant Coordination Bond Lengths (Å) for Na[Gd(CuL)$_4$]·2MeOH·H$_2$O, K[Gd(CuL)$_4$]·3MeOH·H$_2$O, and Cs[Gd(CuL)$_4$]·5H$_2$O$^{a)}$

	Na[Gd(CuL)$_4$]	K[Gd(CuL)$_4$]	Cs[Gd(CuL)$_4$]
Gd(1)–O(1)	2.408(5)	2.429(15)	2.413(10)
Gd(1)–O(2)	2.413(5)	2.358(14)	2.407(10)
Gd(1)–O(5)	2.362(5)	2.359(15)	2.403(7)
Gd(1)–O(6)	2.436(4)	2.405(16)	2.370(8)
Gd(1)–O(9)	2.366(6)	2.351(15)	2.432(13)
Gd(1)–O(10)	2.426(5)	2.414(14)	2.338(9)
Gd(1)–O(13)	2.406(5)	2.439(14)	2.439(8)
Gd(1)–O(14)	2.422(5)	2.333(15)	2.383(8)
Cu(1)–O(3)	2.037(5)	2.020(16)	2.028(10)
Cu(1)–O(4)	1.895(6)	1.850(17)	1.840(11)
Cu(1)–N(1)	1.915(7)	1.886(19)	1.894(13)
Cu(1)–N(2)	1.930(7)	1.93(2)	1.949(11)
Cu(2)–O(7)	1.999(5)	2.005(17)	2.044(9)
Cu(2)–O(8)	1.853(7)	1.841(18)	1.857(8)
Cu(2)–N(3)	1.888(7)	1.880(19)	1.903(10)
Cu(2)–N(4)	1.920(7)	1.93(2)	1.886(11)
Cu(3)–O(11)	1.997(6)	1.993(17)	2.030(10)
Cu(3)–O(12)	1.870(7)	1.840(19)	1.821(10)
Cu(3)–N(5)	1.919(7)	1.865(19)	1.980(11)
Cu(3)–N(6)	1.914(7)	1.89(2)	1.912(11)
Cu(4)–O(15)	2.038(5)	2.033(14)	1.992(9)
Cu(4)–O(16)	1.866(5)	1.854(13)	1.903(10)
Cu(4)–N(7)	1.927(6)	1.850(19)	1.879(12)
Cu(4)–N(8)	1.903(6)	1.89(2)	1.920(11)
Cation–O(1)*		2.903(17)	
Cation–O(2)	2.471(6)	2.867(15)	3.373(9)
Cation–O(6)*	2.406(6)	2.663(17)	
Cation–O(7)**			3.194(8)
Cation–O(8)**			3.192(12)
Cation–O(10)	2.422(6)	2.679(15)	3.022(9)
Cation–O(11)			3.507(10)
Cation–O(13)		2.988(18)	
Cation–O(14)*	2.449(5)	2.846(15)	
Cation–O(17)			3.46(2)
Cation–O(18)			3.130(18)
Cation–O(19)	2.400(10)	3.05(2)	
Dihedral angle between adjacent Cu^{II} coordination planes.			
(Cu1–Cu2)	61.2	64.7	73.6
(Cu2–Cu3)	106.1	107.9	109.3
(Cu3–Cu4)	70.2	69.1	84.8
(Cu4–Cu1)	119.9	114.9	97.6

a) * and ** denote the symmetry operations of ($-x+2$, $y-1/2$, $-z+1/2$) and ($-x+2$, $-y$, $-z$), respectively.

K$^+$–O(oximate) distances in the range of 2.679(15)–2.988(18) Å and one K$^+$–O(methanol) distance of 3.05(2) Å, the Gd–Gd distance of 7.562(1) Å and K–Gd distances of 3.936(5) and 3.927(5) Å. Totally the coordination number of the K$^+$ is seven. Though the potassium salt assumes an isomorphous structure to the sodium salt, these K–Gd distances become longer, because of the larger ionic radii.[10]

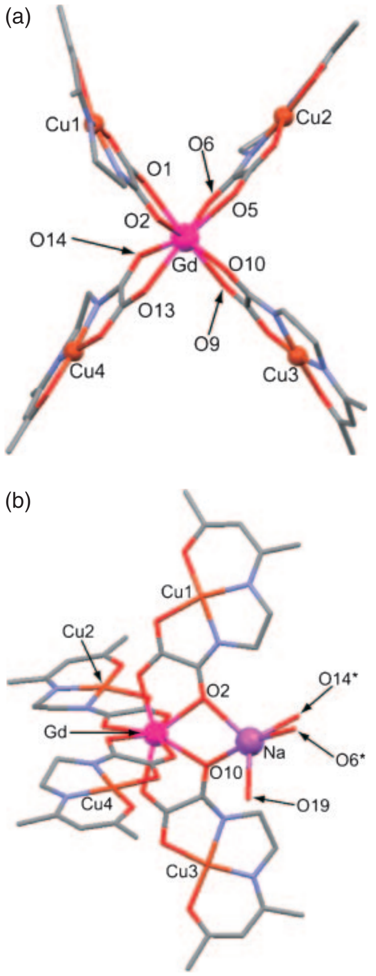

Figure 1. (a) Molecular structure of the anionic part of Na[Gd(CuL)$_4$] with the selected atom numbering scheme, showing a pinwheel-like [Gd(CuL)$_4$]$^-$ core. (b) Molecular structure of Na[Gd(CuL)$_4$] with the selected atom numbering scheme, showing the bridging mode around Na$^+$ ion and the orientation of four (CuL) units around Gd^{3+}.

Structural Descriptions of Cs[Gd(CuL)$_4$]. Figure 3a shows a pentanuclear pinwheel-like GdCu$_4$ core of the anionic part of Cs[Gd(CuL)$_4$], where the central Gd^{III} ion is coordinated by eight oxygen atoms of four ligand-complexes. The eight Gd–O distances are Gd–O(1) = 2.413(10), Gd–O(2) = 2.407(10), Gd–O(5) = 2.403(7), Gd–O(6) = 2.370(8), Gd–O(9) = 2.432(13), Gd–O(10) = 2.338(9), Gd–O(13) = 2.439(8), and Gd–O(14) = 2.383(8) Å, being compatible with the corresponding values of the sodium and potassium salts. Each Cu^{II} complex assumes a square-planar N$_2$O$_2$ coordination geometry and coordinates to Gd^{III} ion by two oxygen atoms at the terminal oximate site as an electrically mononegative chelate ligand. Figure 3b shows the bridging mode around Cs$^+$ ion of Cs[Gd(CuL)$_4$], where a Cs$^+$ ion is coordinated by three oxygen atoms of two (CuL) in a plane and by those of the adjacent [Gd(CuL)$_4$] core, with the distances of Cs–O(2) = 3.373(9), Cs–O(10) = 3.022(9), and Cs–O(11) = 3.507(10) Å. The most striking feature of the cesium salt different from the sodium and potassium salts is the assembly manner of [Gd(CuL)$_4$] cores by Cs$^+$ ions. The assembled structure of [Gd(CuL)$_4$] molecules by Cs$^+$ ions is a cyclic structure {Cs[Gd(CuL)$_4$]}$_2$. Figure 4 shows the cyclic structure of {Cs[Gd(CuL)$_4$]}$_2$, in which two Cs$^+$ ions act as connectors

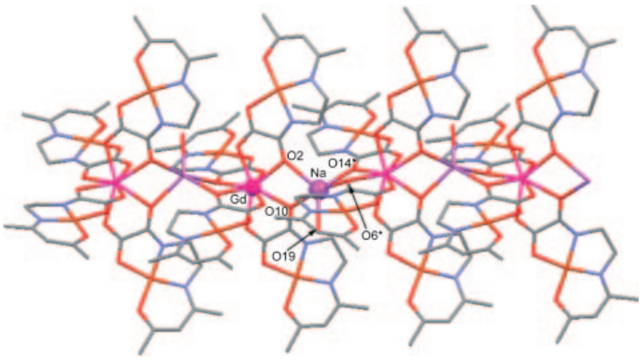

Figure 2. One-dimensional structure of $Na[Gd(CuL)_4]$ consisting of alternately arrayed pinwheel-like $[Gd(CuL)_4]^-$ core and Na^+ ion as connector.

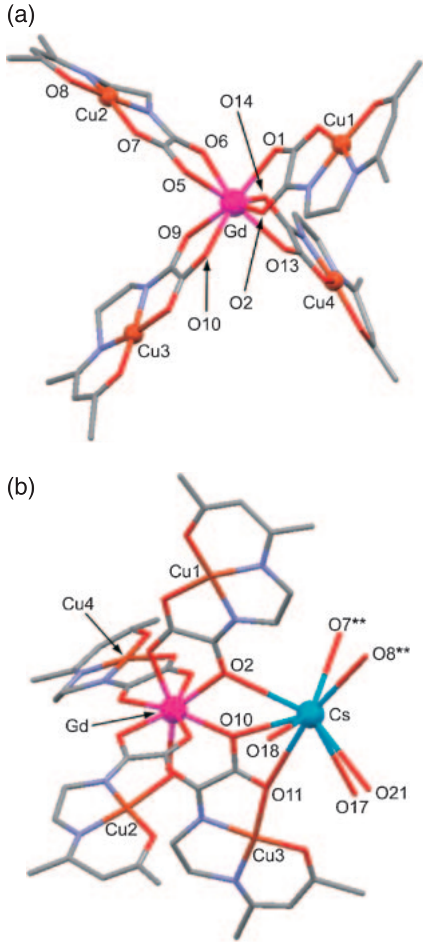

Figure 3. (a) Molecular structure of the anion of $Cs[Gd(CuL)_4]$ with the selected atom numbering scheme, a pinwheel-like $[Gd(CuL)_4]^-$ core. (b) Molecular structure of $Cs[Gd(CuL)_4]$ with the selected atom numbering scheme, showing the bridging mode around Cs^+ ion and the orientation of four (CuL) units around Gd^{3+}.

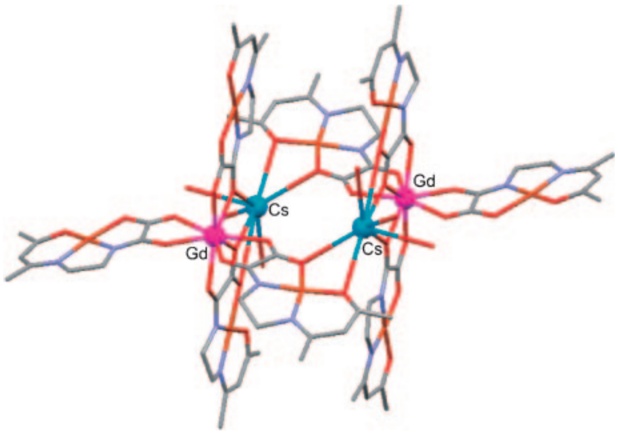

Figure 4. Aggregated molecular structure of $Cs[Gd(CuL)_4]$, showing a cyclic $\{Cs[Gd(CuL)_4]\}_2$ cluster.

of two $[Gd(CuL)_4]$ to make a dinuclear cyclic structure $\{Cs[Gd(CuL)_4]\}_2$, that is definitely different from the 1D structure of the sodium and potassium salts. The cyclic molecule has an inversion center and a Cs^+ ion is bridged by three oxygen atoms of two (CuL) parts with the distances of Cs–O(2) = 3.373(9), Cs–O(10) = 3.022(9), and Cs–O(11) = 3.507(10) Å and two oxygen atoms of a (CuL) of the adjustment core with the distances of Cs–O(7)** = 3.194(8) and Cs–O(8)** = 3.192(12) Å. It is remarkable that O(7) and O(8) atoms of Cu(2) molecule are not of the oximate moiety. Totally the coordination number of the Cs^+ is eight. One of four (CuL) sites has an opposite direction, and that causes structural difference from $Cs[Gd(CuL)_4]$ and $Na[Gd(CuL)_4]$ or $K[Gd(CuL)_4]$ complexes.

The sodium and potassium salts assume a 1D chain structure bridged by Na^+ or K^+ ions, while the cesium salt assumes a cyclic structure bridged by Cs^+ ion. As the ionic size of the cation increases in the order of Na^+, K^+, and Cs^+, the present result implies that the cation size affects the assembly structure 1D infinite or cyclic structure. The most striking difference between 1D and cyclic structures is found in configuration of the four (CuL) of a pinwheel-like $[Gd(CuL)_4]$ core. In the case of 1D structure, two ethylenediamine moieties of two (CuL) molecules in *trans*-sites of a pinwheel core are positioned at the same side, while in the case of the cyclic structure, the two ethylenediamine moieties of one pair of two pairs in *trans*-sites are positioned at the opposite sides, making it possible to form cyclic structure.

Magnetic Properties of $M[Gd(CuL)_4]$ ($M^+ = Na^+$, K^+, and Cs^+). The temperature dependences of the magnetic susceptibilities of $M[Gd(CuL)_4]$ ($M^+ = Na^+$, K^+, and Cs^+) were measured in the temperature range of 2.0–300.0 K under an external magnetic field of 0.5 T. Figure 5 shows the plots of $\chi_M T$ vs. T for three complexes, where χ_M is the molar magnetic susceptibility per $GdCu_4$ unit and T is the absolute temperature. The magnetic behaviors of three complexes are essentially similar to each other. The $\chi_M T$ values at 300.0 K are 9.20, 9.28, and 9.56 $cm^3\,K\,mol^{-1}$ for the Na^+, K^+, and Cs^+ salts, respectively, these values close to the calculated value of 9.375 $cm^3\,K\,mol^{-1}$ expected for four Cu^{II} ($S = 1/2$, $g = 2.00$) and one Gd^{III} ($4f^7$, $J = 7/2$, $L = 0$, $S = 7/2$, $^8S_{7/2}$) non-interacting ions. On lowering the temperature from 300.0 to 2.0 K, the $\chi_M T$ value increases gradually to reach a maximum value, and then decreases abruptly. The increase of the $\chi_M T$ value in the higher temperature region indicates the operation of a ferromagnetic interaction between Cu^{II} and Gd^{III} ions

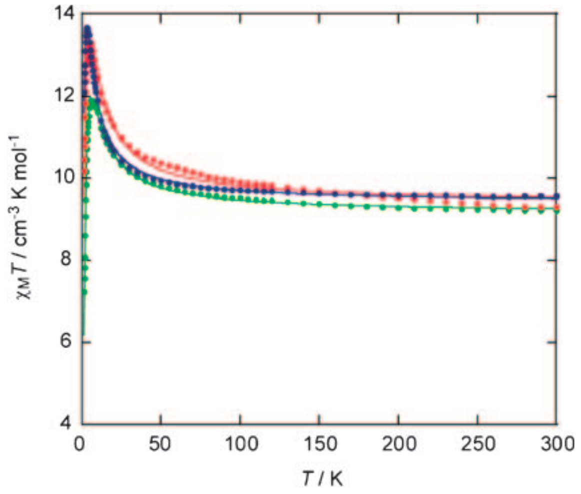

Figure 5. Plots of $\chi_M T$ vs. temperature for three complexes M[Gd(CuL)$_4$] (M$^+$ = Na$^+$(●), K$^+$(●), and Cs$^+$(●)). The solid lines represent the theoretical curves with the best-fit parameters given in the text.

within a pentanuclear pinwheel GdCu$_4$ core and the decrease in the lower temperature region indicates the operation of an antiferromagnetic intercore interaction. The Curie–Weiss plots of $1/\chi_M$ vs. T, are informative to know the intra- and intercore magnetic interactions. The $1/\chi_M$ vs. T plots in the higher temperature range of 50–300 K follow the Curie–Weiss equation of $1/\chi_M = (T - \theta)/C$ with positive Weiss constants of $\theta = +3.75$, $+2.94$, and $+1.58$ K for the Na$^+$, K$^+$, and Cs$^+$ salts, respectively. The $1/\chi_M$ vs. T plots in the lower temperature range below 5 K follow the Curie–Weiss equation with negative Weiss constant of $\theta = -2.6$, -0.96, and -0.22 K for the Na$^+$, K$^+$, and Cs$^+$ salts, respectively. The results from the Curie–Weiss plots are consistent with the coexistence of a relatively strong ferromagnetic and a weaker antiferromagnetic interaction. This also indicates that the negative Weiss constant becomes smaller with the increase of the cation size, demonstrating the intercore antiferromagnetic interaction is affected by the cation size.

The ground state of the Gd^{III} ion is $^8S_{7/2}$ with $J = 7/2$, $L = 0$, and $S = 7/2$, indicating that there is no contribution from orbital angular momentum. Therefore, the present GdCu$_4$ complexes can be described as magnetically isotropic molecules. Thus, the magnetic susceptibility can be reproduced by the equation derived from the spin-only Hamiltonian based on the pentanuclear GdCu$_4$ structure, $\hat{H} = \beta H(4g_{Cu}S_{Cu} + g_{Gd}S_{Gd}) - 2JS_{Gd}(S_{Cu1} + S_{Cu2} + S_{Cu3} + S_{Cu4})$. The best-fit parameters are as follows: Na$^+$ salt, $g_{Gd} = 2.00$(fixed), $g_{Cu} = 2.12$, $J_{Gd\text{–}Cu} = +1.11$ cm^{-1}, $zJ' = -0.065$ cm^{-1}, monomeric impurity of Cu(II) = 0.4%; K$^+$ salt, $g_{Gd} = 2.00$(fixed), $g_{Cu} = 2.13$, $J_{Gd\text{–}Cu} = +1.03$ cm^{-1}, $zJ' = -0.038$ cm^{-1}, monomeric impurity of Cu(II) = 0.2%; Cs$^+$ salt, $g_{Gd} = 2.00$(fixed), $g_{Cu} = 2.14$, $J_{Gd\text{–}Cu} = +0.67$ cm^{-1}, $zJ' = -0.025$ cm^{-1}, monomeric impurity of Cu(II) = 0.2%. The calculated curves with the parameters are drawn in Figure 5. The Gd–Cu coupling constant J is very similar in the Na$^+$ and K$^+$ salts (1.11 and 1.03 cm^{-1}) but is slightly smaller for the Cs$^+$ salt, probably due to the different packing of the GdCu$_4$ clusters in the latter salt; (2) the intercluster antiferromagnetic interaction responsible for the low temperature decrease of $\chi_M T$ significantly decreases when the ionic radius of the alkali cation increases (from Na$^+$ to Cs$^+$) thus keeping the pentanuclear units further apart.

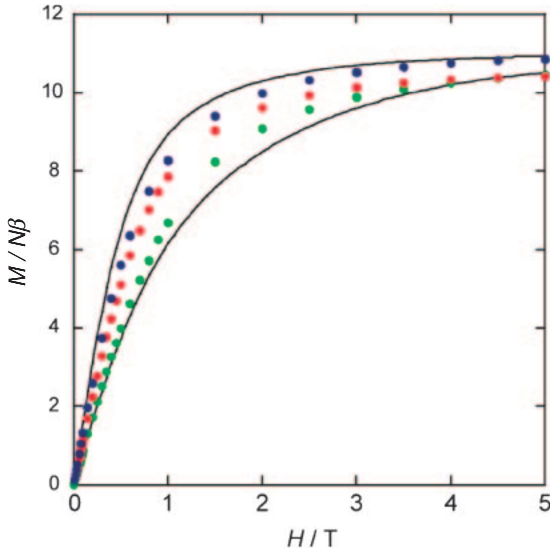

Figure 6. Field dependence of the magnetization of M at 2 K as a function of the applied magnetic field H for M[Gd(CuL)$_4$] (M$^+$ = Na$^+$(●), K$^+$(●), and Cs$^+$(●)). The solid lines represent the theoretical curves for the sum of the Brillouin functions for four Cu^{II} ions ($S_{Cu} = 1/2$) and Gd^{III} ($S_{Gd} = 7/2$) ion with, and $g = 2.00$ and for the Brillouin function of an $S = 11/2$ spin state derived from the ferromagnetic coupled GdCu$_4$.

The field dependence of the magnetization at 2.0 K was measured from 0 to 5 T. The results are plotted in Figure 6 in the form of $M/N\beta$ vs. H and compared with the Brillouin functions calculated for possible spin states for GdCu$_4$ molecule ($S_{Cu} = 1/2$, $S_{Gd} = 7/2$). The experimental curves are lower than the calculated curve of the possible highest spin ground state $S = 11/2$ ($11/2 = 4 \times 1/2 + 7/2$) resulting from the intramolecular ferromagnetic coupling within the molecule of GdCu$_4$ and higher than the curve of magnetically independent four $S_{Cu} = 1/2$ and one $S_{Gd} = 7/2$. The experimental curves are in the order Na$^+$, K$^+$, and Cs$^+$. The temperature- and field-dependent magnetic data both suggest a relatively strong intramolecular antiferromagnetic interaction that can be operating through Na$^+$ ion. The compounds used for the single-crystal X-ray analyses and the magnetic measurements are different in the amount of crystal solvents. The 1D and cyclic structures were fundamentally retained in the present p–d–f molecular system and the magnetic properties can be affected mainly by the assembly structures.

Concluding Remarks

Three copper(II)–gadolinium(III) complexes with M$^+$ = Na$^+$, K$^+$, and Cs$^+$, M[Gd(CuL)$_4$], have been synthesized, where H$_3$L = N-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid. The anionic part [Gd(CuL)$_4$]$^-$ assumes a pentanuclear pinwheel-like GdCu$_4$ core and the central Gd^{III} ion is coordinated by eight oxygen atoms of four (CuL), where each (CuL) assumes a square-planar N$_2$O$_2$ coordination geometry and functions as a bidentate chelate ligand to Gd^{III} ion.

Further, the adjacent pentanuclear cores are connected by the cation. Depending on the size of ionic radii, the assembly structure is determined. The ionic radii given in the reference are $Li^+ = 0.76$ Å, $Na^+ = 1.02$ Å, $K^+ = 1.38$ Å, $Rb^+ = 1.52$ Å, $Cs^+ = 1.67$ Å in the case of coordination number 6. The sodium and potassium salts assume a 1D chain structure bridged by Na^+ or K^+ ions, while the cesium salt assumes a cyclic structure bridged by Cs^+ ion. For both assembly structures, the cation act as a connector between the adjacent $[Ln(CuL)_4]^-$ cores. The magnetic data demonstrated an intramolecular ferromagnetic interaction within a $GdCu_4$ core and an intermolecular antiferromagnetic interaction operating through the cation. Intermolecular antiferromagnetic interaction decreases in the order of the cation size $Na^+ < K^+ < Cs^+$. The present results show that the assembly structure can be tuned by the alkali cation.

Experimental

Materials. All chemicals and solvents used for the synthesis were reagent grade and were obtained from Tokyo Kasei Co., Ltd. and Wako Pure Chemical Industries, Ltd., and used without further purification.

$Na[CuL]\cdot1.33H_2O$. A ligand H_3L was prepared according to a method of Costes, where H_3L is *N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid. A ligand-complex, $Na[CuL]\cdot1.33H_2O$, was prepared according to a method of Costes et al.[8] and confirmed by elemental analysis. Yield: 0.80 g (50%). Anal. Found: C, 33.04; H, 4.31; N, 8.44%. Calcd for $Na[CuL]\cdot1.33H_2O = C_9H_{13.66}N_2O_{5.33}NaCu$: C, 33.60; H, 4.28; N, 8.70%. IR (KBr disk): $\nu_{C=O}$ 1672 cm^{-1}, $\nu_{C=N}$ 1605 cm^{-1}.

$K[CuL]\cdot2.5H_2O$. The potassium salt was prepared according to a similar procedure of the sodium salt, using KOH instead of NaOH. To a solution of ligand H_3L (1.21 g, 5 mmol) in 50 mL of methanol was added an aqueous solution of potassium hydroxide (0.84 g, 15 mmol) in 10 mL of water. To the mixture was slowly added an aqueous solution of copper(II) acetate monohydrate (1.00 g, 5 mmol) in 30 mL of water under stirring. The resulting solution was filtered and then the solvent of the filtrate was reduced to 10 mL by rotary evaporator. To the resulting solution was added 100 mL of acetone and the solution was left to stand for 2 days. Violet needle crystals precipitated were collected by suction filtration. Yield: 1.05 g (62%). Anal. Found: C, 29.92; H, 4.79; N, 7.98%. Calcd for $K[CuL]\cdot2.5H_2O = C_9H_{16}N_2O_{6.5}KCu$: C, 30.12; H, 4.49; N, 7.81%. IR (KBr disk): $\nu_{C=O}$ 1670 cm^{-1}; $\nu_{C=N}$ 1607 cm^{-1}.

$Cs[CuL]\cdot1.33H_2O$. The cesium salt was prepared according to the similar procedure of the sodium salt, using CsOH instead of NaOH. To a solution of ligand H_3L (1.21 g, 5 mmol) in 50 mL of methanol was added an aqueous solution (10 mL) of cesium hydroxide (2.24 g, 15 mmol). To the mixture was added dropwise an aqueous solution (30 mL) of copper(II) acetate monohydrate (1.00 g, 5 mmol) under stirring. The resulting solution was filtered and the solvent of the filtrate was reduced to 10 mL by rotary evaporator. To the resulting solution was added 100 mL of acetone to precipitate purple-red needle crystals. Anal. Found: C, 24.99; H, 3.05; N, 6.56%. Calcd for $Cs[CuL]\cdot1.33H_2O = C_9H_{13.66}N_2O_{5.33}CsCu$: C, 25.04; H, 3.19; N, 6.49%.

$[Gd(hfa)_3(H_2O)_2]$. The gadolinium(III) complex was prepared by mixing $Gd(OAc)_3\cdot nH_2O$ and hexafluoroacetylacetone in 1:3 mol ratio in water according to the literature.[11]

$Na[Gd(CuL)_4]$. A methanolic solution (30 mL) of $Na[CuL]\cdot1.33H_2O$ (0.13 g, 0.4 mmol) was gently poured into a methanolic solution (10 mL) of $[Gd(hfa)_3(H_2O)_2]$ (0.081 g, 0.1 mmol) at ambient temperature. The resulting solution was allowed to stand for several days, during which time blue-purple crystals precipitated and they are collected by suction filtration. Crystals easily loose the crystal solvents and the elemental analysis agrees with the formula of $Na[Gd(CuL)_4]$. Yield: 0.09 g (67%). Anal. Found: C, 33.85; H, 3.62; N, 9.04%. Calcd for $Na[Gd(CuL)_4] = C_{36}H_{44}N_8O_{16}NaCu_4Gd$: C, 33.80; H, 3.47; N, 8.76%. IR (KBr disk): $\nu_{C=O}$ 1655 cm^{-1}, $\nu_{C=N}$ 1596 cm^{-1}.

$K[Gd(CuL)_4]\cdot3H_2O$. $K[Gd(CuL)_4]$ was prepared according to a similar procedure of the synthesis of $Na[Gd(CuL)_4]$, using $K[CuL]\cdot2.5H_2O$ instead of $Na[CuL]\cdot1.33H_2O$. Blue-purple crystals easily lose the crystal solvents. Yield: 0.07 g (57%). Anal. Found: C, 32.08; H, 3.79; N, 8.52%. Calcd for $K[Gd(CuL)_4]\cdot3H_2O = C_{36}H_{50}N_8O_{19}KCu_4Gd$: C, 32.04; H, 3.73; N, 8.30%. IR (KBr disk): $\nu_{C=O}$ 1655 cm^{-1}, $\nu_{C=N}$ 1594 cm^{-1}.

$Cs[Gd(CuL)_4]\cdot6H_2O$. $Cs[Gd(CuL)_4]$ was prepared according to a similar procedure of the synthesis of $Na[Gd(CuL)_4]$ by the use of $Cs[CuL]\cdot1.33H_2O$ instead of $Na[CuL]\cdot1.33H_2O$. Anal. Found: C, 28.91; H, 3.83; N, 7.19%. Calcd for $Cs[Gd(CuL)_4]\cdot6H_2O = C_{36}H_{56}N_8O_{22}CsCu_4Gd$: C, 28.88; H, 3.77; N, 7.48%.

Physical Measurements. Elemental C, H, and N analyses were carried out at the Center for Instrumental Analysis of Kumamoto University. Infrared spectra were recorded at room temperature using a Nicolet Avatar 370 DTGS (Thermo Electron Corporation) spectrometer with samples in KBr disks. Thermogravimetric analyses were carried out on a TG/DTA6200 (SII Nano Technology Inc.) instrument at a 10 K min^{-1} heating rate using ca. 2 mg sample. Temperature-dependent magnetic susceptibilities in the temperature range 2–300 K under an external magnetic field of 0.5 T and field-dependent magnetization measurements in an applied magnetic field from 0 to 5 T at 2 K were measured with an MPMS5 SQUID susceptometer (Quantum Design, Inc.). The calibrations were performed with palladium. Corrections for diamagnetism were applied using Pascal's constants.

X-ray Structure Determination. The crystals tend to decompose due to the elimination of crystal solvents. In order to keep the quality of the crystal, a crystal with a small amount of mother liquid was encapsulated in a glass tube and the X-ray diffraction data were collected at ambient temperature. The X-ray diffraction measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71075$ Å). The structures were solved by direct methods and expanded using Fourier transform. Non-hydrogen atoms were refined anisotropically and hydrogen atoms at their calculated positions were included in the structure factor calculation. Full-matrix least-squares refinement based on the observed reflections ($I > 2.00\sigma(I)$) was employed, where the unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| -$

$|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were used. All calculations were performed using the CrystalStructure crystallographic software package.[12,13]

CCDC-789156–789158 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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