A New Spherical Metallacryptate Compound $[Na\subset\{Cu_6(Thr)_8(H_2O)_2(ClO_4)_4\}]\cdot ClO_4\cdot 5H_2O$: Magnetic Properties and DFT Calculations

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The hexanuclear copper(II) complex with threoninato acid has been synthesized. Its structure can be described as an octahedron cage with D_{2h} symmetry in which six copper ions are bound by eight threoninato acids with a $[3.1_1 2_{23} 1_3 0]$ coordination mode and one Na^+ cation being captured within the center of the cage. In contrast with other hexanuclear copper compounds containing amino acids, the title compound has a prolate Cu_6 octahedron with the longest axial distance and a rectangle equatorial plane, as well as special coordinated perchlorate ions. Compared with classic cryptate, hexanuclear copper(II) compounds with amino acids can be regarded as a new topologic type of spherical macrotricyclic metallacryptates [2,2,2,2] whose cages have a high selectivity for sodium ions. The analysis of magnetic susceptibility data shows that the threoninato compound has a ground state with spin $S = 3$. The computing coupling constant between the equatorial Cu centers and the axial ones is 4.4 cm^{-1}, calculated by using DFT methods for a model compound. This is close to three known experimental values of 1.39, 0.56 or 0.43 cm^{-1} for complexes with 4-hydroxy-L-prolinato, L-prolinato or L-threoninato acid as ligands, respectively. The dominant ferromagnetic interactions for these complexes can be essentially attributed to the orthogonality between the magnetic orbitals, d_{xz} or d_{yz} orbitals for the equatorial Cu^{II} centers and $d_{x^2-y^2}$ orbitals for the axial ones.

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Introduction

The crown ether[1] is one of the classic synthetic ionophores, and the discovery of its cation-binding properties launched the rich field of host-guest chemistry.[2] While increasing the denticity of the crowns through construction of three-dimensional cavities, the cryptands[3] increase the binding affinities of the crowns for alkali metals. Using hydroxamic acid [e.g., salicylhydroxamic acid (SHI)] or oxime as ligands to stabilize the metallacrown ring, Pecoraro[4] synthesized a series of metallacrown analogs by introducing the heteroatom substitution approach which incorporates transition metal ions and nitrogen atoms into the methylene positions of the crown ethers. Once transition metals have been incorporated into metallacrowns they tend to have some interesting properties, which are not found in the simple organic crowns, such as redox activity, strong absorption spectra, and paramagnetism. Pecoraro[5] has obtained a cylindrical metallacryptate $Na[(Na(DMF)_3)_2\{[Na_{0.5}[Ga(SHI)]_4]_2(\mu_2\text{-}OH)_4\}]$, whose $[Na_{0.5}[Ga(SHI)]_4]_2$ metal cycles can be fused together through bridging hydroxides to form bicyclic metallacrowns. The cavity thus formed can selectively bind sodium cations. Another type of the inorganic analogs of cryptates,[6] based on a polyoxometalate framework, shows selectivity for lanthanides.

As the basic building units of proteins, amino acids are ubiquitous and indispensable ligands in biology, and it has been proven that amino acids are excellent ligands for the construction of 3d–4f heteronuclear clusters.[7,8] We[9] have also obtained two hexanuclear copper complexes with two amino acids, glycine (Gly) and L-proline (Pro), respectively, which also have a cavity that binds the sodium cation. Another hexanuclear copper analog with 4-hydroxy-L-proline (hpro) has been synthesized by Winpenny,[10] which is ferromagnetically coupled, yielding an $S = 3$ spin ground state. Bu[11] has produced a one-dimension analog $\{Cu_6Na\}_n$ chain by using 1,5-diazacyclooctane-N,N'-diacetate acid as the ligand. In this paper, we wish to report a new hexanuclear copper complex $[Na\subset\{Cu_6(Thr)_8(H_2O)_2(ClO_4)_4\}]\cdot ClO_4\cdot 5H_2O$ (**1**) with threoninato acid (Thr) as an inorganic analog of cryptands, which binds sodium cations through eight oxygen atoms of the carboxylate groups of eight threoninato acids.

The aims of this work, from a new viewpoint, are to recognize hexanuclear copper compounds with amino acids as a new type of spherical macrotricyclic metallacryptates, and to study the influence of the various ligands on the structure and magnetic properties of this family. Furthermore,

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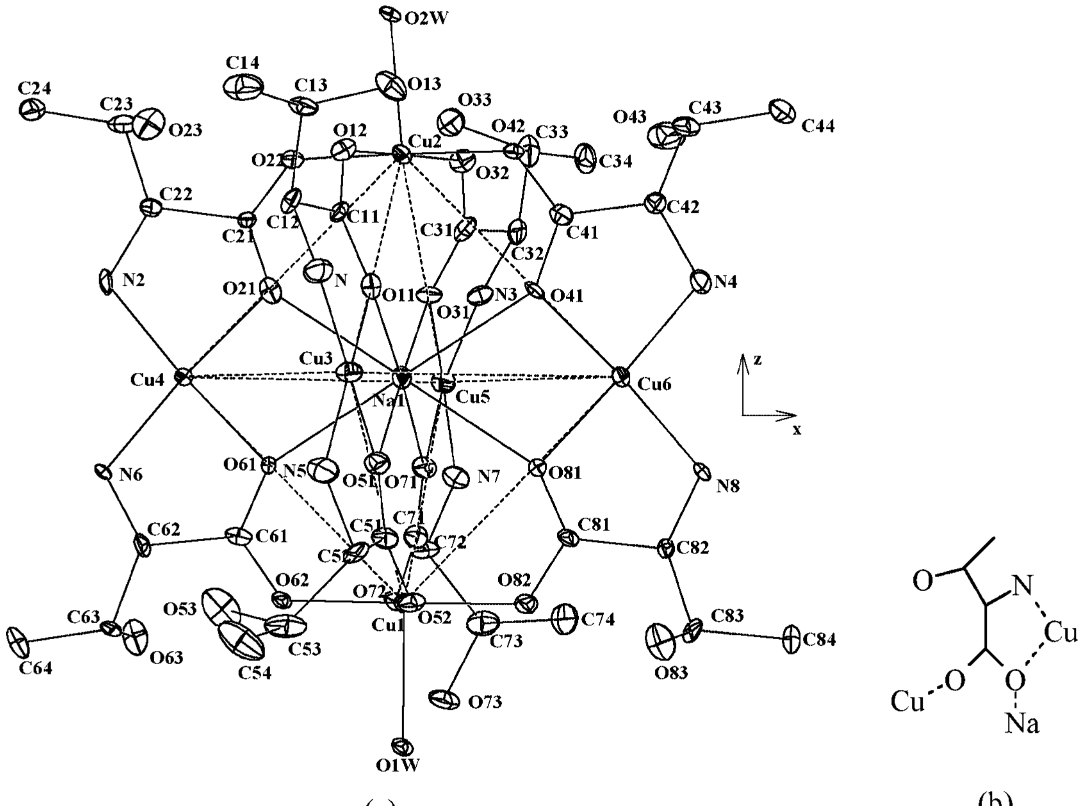
the magnetic properties of these complexes are firstly calculated by employing $\{Cu_6(Gly)_8\}^{4+}$ as a model by using the broken-symmetry approach[12] with density functional theory (DFT). Finally the nature of magnetic exchange for these complexes is explained from the scope of orbital interaction.

Results and Discussion

Structural Description

Part (a) of Figure 1 shows the skeleton structure of **1**. Selected interatomic distances and bond angles for compound **1** are collected in Table 1, respectively. As shown in Figure 1, a Na^+ ion is trapped in the center of a $\{Cu_6(Thr)_8\}$ cage, whose structure may be described as a four-blade propeller. The central metal ion is surrounded by eight carboxylate oxygen atoms which link it to the copper atoms of four $[Cu(Thr)_2]$ units with a mean Na–O distance 2.576 Å. The four units then use their spare carboxylate oxygen atoms to coordinate to the two Cu^{II} centers at the axial vertices, respectively (each Cu^{II} center coordinates to four carboxylate oxygen atoms and the mean Cu_a–O distance is about 1.959 Å). The square pyramidal configuration of the axial Cu^{II} atom is completed by the coordination of a water molecule from the apical position (Cu_a–O_w distances are 2.246 and 2.290 Å, respectively). If the weak interaction is not considered, each equatorial Cu^{II} ion of the cluster has a coordination number (CN) of four and its coordination geometry can be described as square planar. The average Cu_e–O and Cu_e–N distances are 1.949 Å and 1.971 Å, respectively. The six Cu^{II} centers of this cluster form an octahedron with idealized D_{2h} symmetry, the sodium ion being therefore approximately octahedrally surrounded by copper. The four equatorial Cu atoms provide a rectangular plane of the octahedron with two side lengths (the nearest Cu_e–Cu_e distances) of 5.162 and 4.789 Å, but not a square plane as in other amino acid compounds.[9,10] The average distance between axial and equatorial copper atoms is 5.012 Å. Although threoninato acid is a tetradentate ligand, it actually acts as a tridentate ligand by utilizing its amino and carboxylate groups to chelate one Cu^{II} ion and bridge another, as shown in part (b) of Figure 1. The coordination mode indicated by the Harris notation[13] is $[3.1_{1}2_{23}1_{3}0]$.

Four of the five perchlorate ions lie between the propellers formed by the four $[Cu(Thr)_2]$ units as shown in Figure 2. Because the structure of the $[Cu_6]$ unit is distorted, these four perchlorate ions, as the linkages, are not symmetrically equivalent, so that the four Cu^{II} atoms located at the equatorial vertices of a non-binding octahedron provide a rectangular plane, not a square one as for other amino acid compounds. Two oxygen atoms from half of these ions are weakly coordinated to two Cu centers from $[Cu(Thr)_2]$ units, occupying the axial positions of their tetragonally



(a) (b)

Figure 1. (a) ORTEP view of **1** shows the coordination geometries of Cu^{II} and threoninato acid with vibration ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. (b) The coordination mode $[3.1_{1}2_{23}1_{3}0]$ of threoninato ligand indicated by the Harris notation.

Table 1. Selected distances between atoms [Å] and bond angles [°].

Cu(1)–O(52)	1.964(3)	Na(1)–O(11)	2.564(3)	O(31)–Cu(5)–O(71)	92.50(11)
Cu(1)–O(62)	1.944(3)	Na(1)–O(21)	2.557(3)	O(31)–Cu(5)–N(3)	83.84(12)
Cu(1)–O(72)	1.979(3)	Na(1)–O(31)	2.597(3)	O(71)–Cu(5)–N(3)	169.93(13)
Cu(1)–O(82)	1.941(3)	Na(1)–O(41)	2.543(3)	O(31)–Cu(5)–N(7)	174.97(13)
Cu(1)–O(1W)	2.290(2)	Na(1)–O(51)	2.588(3)	O(71)–Cu(5)–N(7)	82.47(12)
Cu(2)–O(12)	1.961(3)	Na(1)–O(61)	2.555(3)	N(3)–Cu(5)–N(7)	101.13(13)
Cu(2)–O(22)	1.958(3)	Na(1)–O(71)	2.587(3)	O(41)–Cu(6)–O(81)	92.22(10)
Cu(2)–O(32)	1.961(3)	Na(1)–O(81)	2.616(3)	O(41)–Cu(6)–N(4)	84.71(12)
Cu(2)–O(42)	1.965(3)	O(82)–Cu(1)–O(62)	178.15(11)	O(81)–Cu(6)–N(4)	175.69(15)
Cu(2)–O(2W)	2.246(2)	O(82)–Cu(1)–O(52)	90.30(12)	O(41)–Cu(6)–N(8)	175.07(12)
Cu(3)–O(11)	1.958(3)	O(62)–Cu(1)–O(52)	87.98(11)	O(81)–Cu(6)–N(8)	83.41(12)
Cu(3)–O(51)	1.951(3)	O(82)–Cu(1)–O(72)	90.53(11)	N(4)–Cu(6)–N(8)	99.77(13)
Cu(3)–N(1)	1.965(3)	O(62)–Cu(1)–O(72)	91.19(11)	O(41)–Na(1)–O(61)	178.01(11)
Cu(3)–N(5)	2.005(4)	O(52)–Cu(1)–O(72)	178.79(11)	O(41)–Na(1)–O(21)	114.12(10)
Cu(4)–O(21)	1.952(3)	O(82)–Cu(1)–O(1W)	90.50(10)	O(61)–Na(1)–O(21)	66.23(9)
Cu(4)–O(61)	1.958(2)	O(62)–Cu(1)–O(1W)	89.99(10)	O(41)–Na(1)–O(11)	74.31(9)
Cu(4)–N(2)	1.954(3)	O(52)–Cu(1)–O(1W)	84.43(10)	O(61)–Na(1)–O(11)	104.11(10)
Cu(4)–N(6)	1.981(3)	O(72)–Cu(1)–O(1W)	96.45(10)	O(21)–Na(1)–O(11)	72.40(9)
Cu(5)–O(31)	1.922(2)	O(22)–Cu(2)–O(32)	93.71(12)	O(41)–Na(1)–O(71)	108.04(10)
Cu(5)–O(71)	1.952(3)	O(22)–Cu(2)–O(12)	88.37(12)	O(61)–Na(1)–O(71)	73.56(9)
Cu(5)–N(3)	1.953(3)	O(32)–Cu(2)–O(12)	177.60(12)	O(21)–Na(1)–O(71)	105.63(10)
Cu(5)–N(7)	1.981(3)	O(22)–Cu(2)–O(42)	178.78(11)	O(11)–Na(1)–O(71)	177.50(11)
Cu(6)–O(41)	1.944(2)	O(32)–Cu(2)–O(42)	86.59(11)	O(41)–Na(1)–O(51)	106.06(11)
Cu(6)–O(81)	1.951(3)	O(12)–Cu(2)–O(42)	91.30(11)	O(61)–Na(1)–O(51)	72.07(10)
Cu(6)–N(4)	1.964(3)	O(22)–Cu(2)–O(2W)	86.32(10)	O(21)–Na(1)–O(51)	108.49(10)
Cu(6)–N(8)	1.977(3)	O(32)–Cu(2)–O(2W)	91.96(11)	O(11)–Na(1)–O(51)	64.93(9)
Cu(1)–Cu(2)	7.1331(8)	O(12)–Cu(2)–O(2W)	89.36(11)	O(71)–Na(1)–O(51)	114.74(10)
Cu(1)–Cu(3)	5.0017(7)	O(42)–Cu(2)–O(2W)	94.85(10)	O(41)–Na(1)–O(31)	72.63(9)
Cu(1)–Cu(4)	5.0498(7)	O(51)–Cu(3)–O(11)	90.06(11)	O(61)–Na(1)–O(31)	109.25(10)
Cu(1)–Cu(5)	5.0631(7)	O(51)–Cu(3)–N(1)	174.15(14)	O(21)–Na(1)–O(31)	72.78(9)
Cu(1)–Cu(6)	4.9778(7)	O(11)–Cu(3)–N(1)	84.55(13)	O(11)–Na(1)–O(31)	115.06(10)
Cu(2)–Cu(3)	5.0596(7)	O(51)–Cu(3)–N(5)	85.44(13)	O(71)–Na(1)–O(31)	65.34(9)
Cu(2)–Cu(4)	4.9722(7)	O(11)–Cu(3)–N(5)	174.78(13)	O(51)–Na(1)–O(31)	178.53(11)
Cu(2)–Cu(5)	4.9675(7)	N(1)–Cu(3)–N(5)	99.83(15)	O(41)–Na(1)–O(81)	65.91(8)
Cu(2)–Cu(6)	5.0013(7)	O(21)–Cu(4)–N(2)	84.39(12)	O(61)–Na(1)–O(81)	113.78(9)
Cu(3)–Cu(4)	4.7017(7)	O(21)–Cu(4)–O(61)	91.16(10)	O(21)–Na(1)–O(81)	178.92(12)
Cu(3)–Cu(6)	5.1685(8)	N(2)–Cu(4)–O(61)	173.54(13)	O(11)–Na(1)–O(81)	108.58(10)
Cu(4)–Cu(5)	5.1554(8)	O(21)–Cu(4)–N(6)	174.92(11)	O(71)–Na(1)–O(81)	73.41(9)
Cu(5)–Cu(6)	4.8753(8)	N(2)–Cu(4)–N(6)	100.51(12)	O(51)–Na(1)–O(81)	72.46(9)
		O(61)–Cu(4)–N(6)	84.06(11)	O(31)–Na(1)–O(81)	106.29(10)

elongated octahedral environment, which gives a long side of the rectangle (5.162 Å). The other ClO_4^- ions, however, bind to two Cu^{II} atoms through only one O-donor of its oxygen atoms, which supplies a short side (4.789 Å). As the location barrage, the distances between the Cu_e and O atoms of single-O-donor perchlorate ions are longer than those between the Cu_e and O atoms of two-O-donor ones. The four perchlorate ions act as the fixed interaction of propellers, which makes the skeleton of **1** more stable. The fifth ClO_4^- ion and several water molecules in the periphery have large thermal parameters in contrast with the skeleton atoms.

Some parameters for hexanuclear copper compounds with different amino acids are collected in Table 2. Different ligands lead to the large structural differences, including space group, shape of the octahedron, axial ligand and coordination modes of the perchlorate ions. *catena*-$[Na{\subset}Cu_2\{Cu(hpro)_2\}_4(ClO_4)_5]\cdot 4H_2O$ is a one-dimensional compound based on the $\{NaCu_6\}$ unit with hydroxyl groups from hpro ligands as the bridge, whereas others are zero-dimensional clusters with solvents, OH^- or perchlorate ions as axial ligands. In glycine complexes, there are two different $\{Cu_6Na\}$ units, one of them with one more Na^+ ion outside the cage. The hpro compound has a compressed octahedron with the shortest axial Cu_a–Cu_a distance forming the chain, while complex **1** has a prolate octahedron with the longest axial distance and a rectangle equatorial plane occurring with the perchlorate ions at the corners. From the Na–O distances, it can be seen that the size and inclusion ability of these octahedron cages are uniform, even though there are many distinctions among the hexanuclear compounds with various amino acids.

New Spherical Metallacryptate [2,2,2,2]

Figure 3 shows that on substituting the Cu_a–O linkage for the bridging N–C units of the classical cryptate [2,2,2] and the O–Cu_e–O linkage for the $[OCH_2CH_2O]$ units, because of their similar O–O distance (2.79 and 2.73 Å,[14] respectively), hexanuclear copper(II) compounds with amino acids can be seen as a new type of spherical macrotricyclic metallacryptate [2,2,2,2]. The four equatorial Cu^{II} ions are a way of bringing the eight oxygen atoms into the

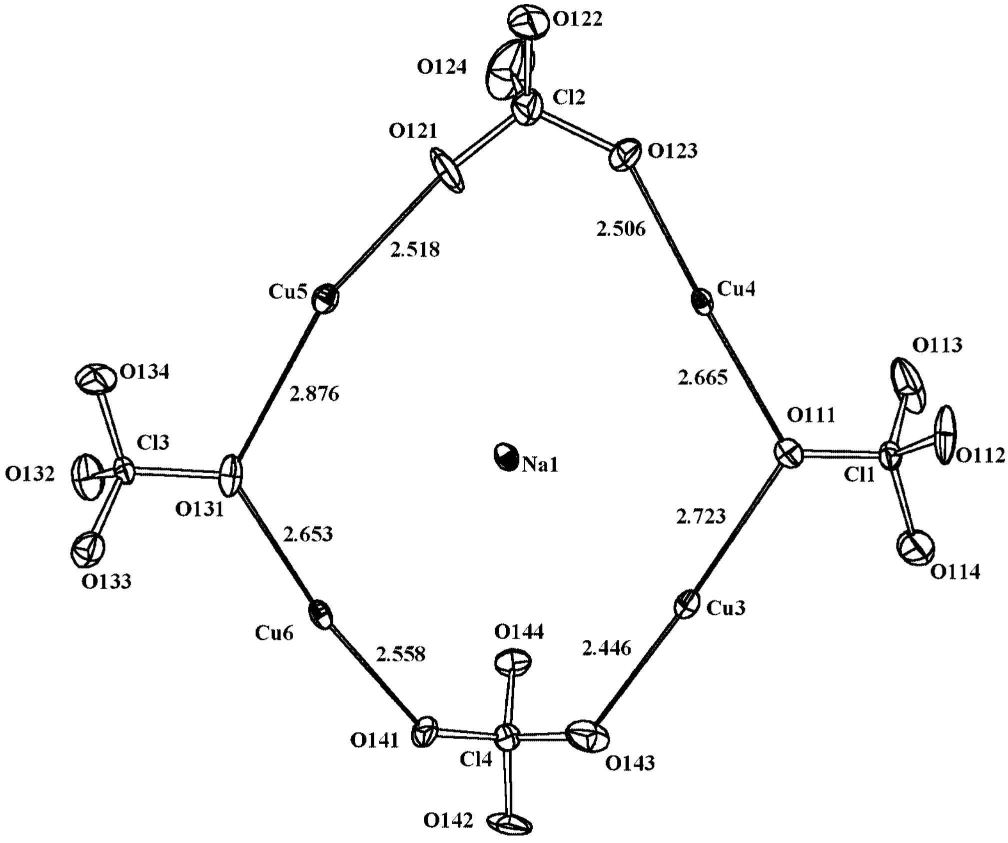


Figure 2. Coordination modes of the four perchlorate ions and the distances [Å] between equatorial Cu^{II} atoms and coordination oxygen atoms of perchlorate ions with vibration ellipsoids at the 30% probability level.

right positions to function as a non-metal cryptate that binds the center sodium cation, while the two axial metal ions use the directionality of the d orbitals to bring the ligands into a definite geometry as the bridging N atoms in the cryptate. The employment of d orbitals results in the enhancement of the connection number of the bridging atoms from three to four. Subtracting the shortest diagonal O–O distance of the cage (O41–O61, 5.098 Å) with the double bonding radii of the oxygen atoms (2 × 1.16 Å),[15] we can estimate that the cavity radius of compound **1** is 1.39 Å, similar to the ionic radius (1.32 Å[16]) of the Na^+ cation with a coordination number (CN) of eight. Winpenny et al.[10] has considered that this kind of cage can selectively bind the Na^+ cation even in the presence of excess Li^+, K^+, Ca^{2+}, La^{3+} or Lu^{3+}, whose ionic radii with a CN of eight are 1.06, 1.65, 1.26, 1.30 and 1.12 Å, respectively.[16] We have still obtained the title compound even in the presence of excess Y^{3+} (1.16 Å)[16] or trivalent rare earth ions. The cryptate [2,2,2], with a cavity size of 1.4 Å, can bind many kinds of metal ions besides alkali or alkaline earth metals to form complexes.[17] The replacement of the bridging N atoms with metal atoms increases the connection number of bridging atoms and thus alters the topological structure of the cryptate, which can further improve the selectivity of the cavity to sodium.

Magnetochemistry

Temperature-dependent magnetic susceptibilities of **1** are measured from ground crystalline samples in the temperature ranges of 4–300 K under a constant magnetic field of 10000 G and are shown in Figure 4 in the forms of χ_m vs. T and $\chi_m T$ vs. T per Cu_6 unit. At room temperature (300 K), the $\chi_m T$ value is 1.7 emu mol^{-1} K for **1**, compared with the expected values 2.25 emu mol^{-1} K for six spin-only Cu^{II} ions ($S = 1/2$, $g = 2$). The difference may result from the diamagnetic contribution of the compound. Upon cooling, **1** shows a continuous slight increase in $\chi_m T$, and a subsequent much sharper increase below ca. 25 K, suggesting that overall **1** is ferromagnetic, as confirmed by the positive Weiss constant (10.8 K). In order to investigate the exchange interaction of **1**, a model Heisenberg Spin-Hamiltonian is employed [Equation (1)].

$$H = -2J'(S_1 + S_2)(S_3 + S_4 + S_5 + S_6) \qquad (1)$$

J' is the exchange coupling constant between the equatorial Cu atoms and the axial Cu ones, and S_i is the spin operator of each Cu center whose suffix is identical to that shown in Figure 1. From the model and the Van Vleck equation,[18] the molar susceptibilities of **1** can be deduced

Table 2. Coupling constants and some structural parameters for hexanuclear Cu^{II} complexes with different amino acids (the unit for bond lengths is Å).

Amino Acids	Gly (ref.[9])	Pro (ref.[9])	Pro (ref.[10])	Hpro (ref.[10])	Thr (this work)
Molecular formula	$Na[NaCu_6(Gly)_8(H_2O)_2]$-$(ClO_4)_6{\cdot}2H_2O$	$[NaCu_6(Pro)_8(OH)]$-$(ClO_4)_4{\cdot}H_2O$	$[Na{\subset}Cu_2\{Cu(Pro)_2\}_4$-$(ClO_4)_5CH_3OH]{\cdot}H_2O$	*catena*-$[Na{\subset}Cu_2\{Cu(hpro)_2\}_4$-$(ClO_4)_5]{\cdot}4H_2O$	$[Na{\subset}\{Cu_6(Thr)_8(H_2O)_2\}]$-$(ClO_4)_5{\cdot}5H_2O$
Space group	$P\bar{1}$	$I4$	$I4$	$P2_1$	$P2_1$
Symmetry	Pseudocubic O_h	D_{4h}	D_{4h}	Idealized D_{4h}	D_{2h}
Bond lengths					
Cu_e–O	1.952	1.952	1.933	1.942	1.949
Cu_e–N	1.995	1.995	1.994	2.006	1.972
Na–O	2.604	2.552	2.546	2.563	2.576
Cu_a–Cu_a	7.115	7.021	7.011	6.998	7.133
Cu_e–Cu_e	5.052	5.000	4.991	5.041	5.162, 4.789
Cu_a–Cu_e	5.041	4.983	4.974	4.996	5.012
Axial ligand and its mean coordination bond lengths	H_2O (2.353)	OH^- (2.314) H_2O (3.612)	Perchlorate ion (2.390) CH_3OH (2.220)	Hydroxyl groups from hpro (2.312)	H_2O (2.268)
Coordination modes of perchlorate ions	In its cell, there are two different $\{Cu_6Na\}$ units with three kinds of perchlorate ions. Two oxygen atoms from six ions are coordinated to two Cu centers, whereas two ions of the second kind only bind to one Cu center through a single O-donor. The other four ions just bind to the peripheral Na^+ cation.	Four ions are symmetrically equivalent. Two oxygen atoms from each ion are coordinated to two Cu centers, respectively.	Four ions are symmetrically equivalent. Two oxygen atoms from each ion are coordinated to two Cu centers, respectively. The fifth ion is coordinated to an axial Cu atom.	Two oxygen atoms from three ions are coordinated to two Cu centers, whereas the fourth ion binds to one Cu through two of its oxygen atoms, and to another with one O-donor.	Two oxygen atoms from two ions are coordinated to two Cu centers, whereas the others bind to two Cu centers with only single O-donors.
The coupling constant J' [cm^{-1}]			+0.56	+1.39	+0.43

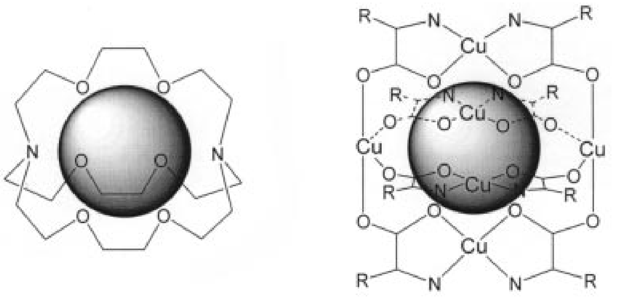


Figure 3. The classic cryptate [2,2,2] (left) and spherically metallacryptate [2,2,2,2] (right). The latter has macrotricycles made up of four blades and the equatorial cycle of perchlorate ions as shown in Figure 2 as an example. The central sphere represents a sodium cation. R is the substitution group of the amino acids or H atom for glycine.

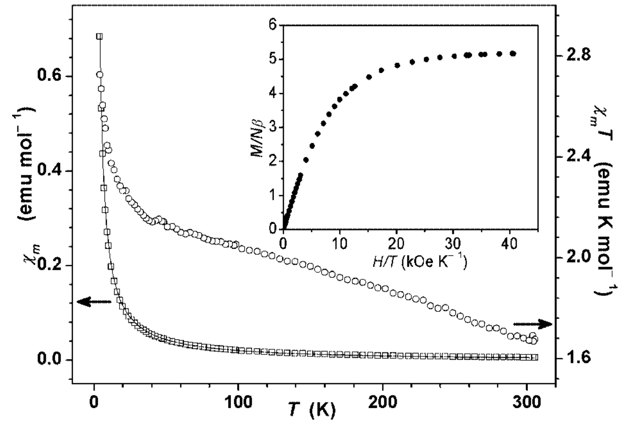


Figure 4. Plot of experimental χ_m vs. T (left) and $\chi_m T$ vs. T (right) for compound **1**. The solid line represents the fitted results. In the inset is a plot of $M/N\beta$ vs. H/T for **1** indicating the spin ground state, $S_T = 3$.

as in Equation (2) with the addition of the sample's diamagnetic contribution χ_{dia} by use of the Kambe vector coupling method,[19] which originates from a total of 20 spin states ranging in spin values from 0 to 3.

$J = J'/k$, and k is the Boltzmann constant, g the Landé factor. After the best least-squares fit to the experimental data, the parameters are given as: $g = 2.01$, $J' = 0.43\ cm^{-1}$ and $\chi_{dia} = -2.60\ (10^{-3}\ emu\,mol^{-1})$ with a final agreement factor $R = 2.32\times10^{-6}$ [$R = \Sigma(\chi_m^{obsd.} - \chi_m^{calcd.})^2/\Sigma(\chi_m^{obsd.})^2$].

Attempts to fit the data by employing the method proposed by Belorizky[20] for octahedron clusters, which includes the coupling between the equatorial metal ions as

$$\chi_m = \frac{3}{8}\times\frac{g^2[28\exp(4J/T) + 30\exp(2J/T) + 16\exp(-2J/T) + 2\exp(-6J/T) + 20]}{T[7\exp(4J/T) + 15\exp(2J/T) + 14\exp(-2J/T) + 3\exp(-4J/T) + 3\exp(-6J/T) + 22]} + \chi_{dia} \tag{2}$$

well as the next nearest interactions, gives the same values for g, J' and χ_{dia} as above. But the next nearest interactions and the coupling through the perchlorate ions are so small that they can be regarded as negligible. The coupling constant of **1** agrees with that of the prolinato compound,[10] 0.56 cm^{-1}. The positive J' value indicates that **1** has a ground state with spin $S = 3$, which is also proven by the $M/N\beta$ vs. H/T plot in the inset of Figure 4 with a saturation value for $M_S/N\beta$ of about 5.2.

DFT Studies

The computational strategy adopted in previous theoretical studies[21] for exchange coupling binuclear complexes is adapted to the hexanuclear complexes by using an approach that Ruiz[22] proposed. The approach consists of evaluating the exchange coupling constant J_{ij} between two paramagnetic metal centers i and j in the hexanuclear molecule by calculating the energy difference between the triplet and broken-symmetry states of a model molecule in which metal atoms are substituted by diamagnetic Zn^{2+} cations in all positions but i and j. Then the coupling constant is given below by employing a phenomenological Heisenberg Hamiltonian $H_{ij} = -2J_{ij}\cdot S_i\cdot S_j$;

$$J_{ij} = \frac{E_{\text{BS}} - E_{\text{TS}}}{S(S+1)} = \frac{E_{\text{BS}} - E_{\text{TS}}}{2} \tag{3}$$

where the total spin $S = S_1 + S_2 = 1$ for the triplet state, and the energy of the broken-symmetry solution is taken as an approximation to that of the singlet state. The procedure keeps with the proposal of Perdew and co-workers,[23] who suggest that the broken-symmetry single determinant is the correct solution of the Kohn–Sham equations for the singlet state. The triplet energy of the model compounds is gained from the single point energy calculation with the convergence parameter 10^{-8}. The energy of the broken-symmetry states is obtained by investigating the stability of the singlet solution with respect to a symmetry-broken solution, which is carried out by means of the formalism developed by Bauernschmitt and Ahlrichs,[24] as implemented in *Gaussian* 03[25] by the keyword STABLE with the option OPT. If the singlet B3LYP solution is unstable, the program finds the symmetry-broken B3LYP solution, which yields the energy of broken-symmetry states.

In order to simplify the computing work and make the theoretical result representative, the $\{Cu_6(Gly)_8\}^{4+}$ is employed as a model to investigate the magnetic properties of hexanuclear Cu$^{\text{II}}$ compounds with amino acids. Its structural data are obtained from CCDC-165331. Because of the symmetry, the coupling constants J_{ij} are only calculated for $i = 1$. After metal atoms are replaced with diamagnetic Zn^{2+} cations in all positions but i and j, the four values of J_{ij} are obtained from equation (c) as shown in Table 3. All of them are positive, indicating that the interaction between the axial copper atoms and the equatorial ones is ferromagnetic. The average value, +4.4 cm^{-1}, is near to three known sets of experimental data, 1.39, 0.56 or 0.43 cm^{-1} for complexes with hpro, Pro or Thr as ligands, respectively.

Table 3. Exchange coupling constants J_{ij} (cm^{-1}) and energies (a.u.) of the triplet (E_{TS}) and broken-symmetry states (E_{BS}) for the $\{Cu_2Zn_4(Gly)_8\}^{4+}$ model compounds. 1 and 2 represent the two axial metal atoms and 3 to 6 the four equatorial ones, respectively.

i,j	E_{BS}	E_{TS}	J_{ij}
1,3	–12665.6168369	–12665.6167647	7.9
1,4	–12665.6186476	–12665.6185943	5.8
1,5	–12665.6181018	–12665.6180721	3.2
1,6	–12665.6168756	–12665.6168696	0.6

Exchange coupling in carboxylate-bridge complexes is largely determined by the conformation of the bridge and the interaction between the d orbitals of the metal and the bridge.[26] As has been shown in the few well-characterized Cu$^{\text{II}}$ complexes bridged by *syn-anti* carboxylate groups, a *syn-anti* conformation of the (Cu–O–C–O′–Cu′) bridge is unfavorably oriented to give a strong overlap between the magnetic orbitals of the copper atoms.[27] For dinuclear copper carboxylates, the magnetic orbitals belong to the Cu $d_{x^2-y^2}$ orbital.[28] But for the hexanuclear Cu$^{\text{II}}$ complexes with amino acids, the coordination geometry around each equatorial Cu$^{\text{II}}$ ion is an elongated octahedron, the Cu$^{\text{II}}$ unpaired electron can be mainly described by the d_{xz} or d_{yz} metallic orbital defined by the short bonds of the Cu–amino acid units; the x and z direction is shown in part (a) of Figure 1. Whereas the coordination geometry around each axial copper(II) ion is a square pyramid with their magnetic orbitals primarily being ascribed to the $d_{x^2-y^2}$ metallic orbital. The planes of the magnetic orbitals d_{xz} or d_{yz} of the equatorial Cu$^{\text{II}}$ ions are nearly perpendicular to those of the $d_{x^2-y^2}$ planes of the two axial Cu$^{\text{II}}$ ions, which provides a favorable orientation for the orthogonality of the magnetic orbitals, thus causing a dominant ferromagnetic interaction. The values of the magnetic coupling for these amino acid compounds are within those observed in the copper complexes[26,29,30] with bridging *syn-anti* carboxylate groups (0.37–14 cm^{-1}).

Experimental Section

General: All starting materials are of reagent grade and used without further purification. Elemental analyses were carried out by the Elemental Analysis Lab of our Institute. Magnetic measurements were carried out with a Quantum Design PPMS model 6000 magnetometer.

Synthesis of 1: $Cu(ClO_4)_2\cdot 5H_2O$ (0.353 g, 1 mmol) was dissolved in 10 mL of H_2O, followed by the addition of threonine (0.119 g, 1 mmol). The pH value of the above solution was then carefully adjusted by slow addition of 0.1 M aqueous NaOH until the precipitate that had formed remained (pH ≈ 5.5). The mixture was then filtered and the filtrate was placed in a desiccator with phosphorus pentoxide. Blue prismatic crystals were obtained several weeks later and isolated by filtration, washed with cold water, and dried in the air. Yield 0.11 g (44.6% based on threonine). $C_{32}H_{78}Cl_5Cu_6N_8NaO_{51}$ (1972.50): calcd. C 19.49, H 3.99, N 5.68; found C 19.26, H 3.83, N 6.09.

Structure Determination and Refinement: A blue prismatic single crystal with approximate dimensions of 0.20 mm × 0.15 mm

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× 0.10 mm was mounted on a glass fiber. X-ray diffraction intensity data were collected on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) by using an ω scan mode at 130.15 K. A total of 22772 reflections were collected within $3.01 \leq \theta \leq 25.03°$, yielding 9896 unique reflections (R_{int} = 0.0621), of which 8718 were considered as observed ($I > 2\sigma(I)$). The crystal structure was solved by direct methods with the Siemens *SHELXTL^{TM}* version 5 package of crystallographic software[15] and refined by full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on all carbon and nitrogen atoms were generated symmetrically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. The final $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, and $Rw = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2\}^{1/2}$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$). The crystallographic data are summarized in Table 4.

CCDC-252441 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.

Computational Details: All calculations have been performed by means of the *Gaussian* 03 suite of ab initio programs[25] using the B3LYP DFT method in which Becke's hybrid exchange functional[31] and the correlation functional[32] of Lee, Yang, and Parr are combined. A basis set of triple-ζ quality[33] is used for the Cu and Zn atoms and of double-ζ quality[34] for other atoms in all calculations.

Table 4. Crystal data collection and structural refinement parameters for **1**.

Empirical formula	$C_{32}H_{78}Cl_5Cu_6N_8NaO_{51}$
Formula mass	1972.50
Crystal appearance	blue prism
Crystal size [mm]	0.20 × 0.15 × 0.10
Crystal system	monoclinic
Space group	*P*2(1)
Unit cell dimensions	
a [Å]	11.6818(10)
b [Å]	23.2158(19)
c [Å]	13.0804(12)
β [°]	94.781(5)
V [Å^3]	3535.1(5)
Z	2
μ [mm^{-1}]	2.083
θ range for data collection [°]	3.01 to 25.03
h, *k*, *l* range	–13 to 13, –22 to 27, –15 to 15
Max./min. transmission	0.9183 to 1.0000
D_c [g cm^{-3}]	1.853
F(000)	2008
Measured reflections	22772
Independent reflections	9896
Observed reflections ($I > 2\sigma(I)$)	8718
R_{int}	0.0621
Parameters refined	928
Goodness of fit on F^2	1.073
R[a]	0.0779
Rw[b]	0.1936
Max./mean shift in the final cycle	0.001/0.000
Max./min. $\Delta\rho$ [e Å^3]	2.437/–1.490

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, [b] $Rw = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma w[(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3]$, a = 0.1110, b = 14.4871.

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