Synthesis, Structure, and Magnetic Property of Linear Chloro-Bridged Nickel(II) Tetramer with Dinucleating Bis-dimethylcyclam Ligand

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A new nickel(II) complex with the composition of $Ni_2Cl_2(L)(ClO_4)_2\cdot 1.5H_2O$ ($L=\alpha,\alpha'$-bis(5*R*(*S*),7*S*(*R*)-5,7-dimethyl-1,4,8,11-tetraazacyclotetradecan-6-yl)-*o*-xylene) has been prepared via a four coordinate complex $[Ni_2(L)](ClO_4)_4\cdot 3H_2O$ from $[Ni_2(\mu\text{-Br})Br_2(L)]Br\cdot H_2O$. The compound crystallizes in orthorhombic space group $Ccm2_1$ with cell parameters at −80 °C, a=21.90(1), b=20.28(1), c=19.63(1) Å, V=8718(1) Å^3, Z=8. The crystal consists of the cationic dinuclear unit $[Ni_2(\mu\text{-Cl})Cl_2(L)]^+$, the counter anion ClO_4^-, and water of crystallization. In $[Ni_2(\mu\text{-Cl})Cl_2(L)]^+$, three chloride ions and two nickel ions are alternately arranged in an almost linear manner, and two cyclam rings with the most stable *trans*-III type conformation are arranged in a face-to-face manner. This cationic dinuclear unit is further connected to each other by sharing the terminal Cl ligand to form pseudo one-dimensional chain structure of the ···Cl–Ni–Cl–Ni–Cl··· type. However, one of the Cl atoms which bridges the dinuclear units is statistically disordered at two positions along the chain and thereby the repeating unit in the chain is a chloro bridged dimer of the dinucleating ligand complex. The neighboring Ni–Cl distances range from 2.568(4) to 2.855(4) Å. The temperature dependent magnetic behavior in the range of 25—300 K has been interpreted by the usual Heisenberg–Dirac–Van Vleck model, assuming that only three Ni(II) ions in $\{Ni_2Cl_2(L)\}_2$ are paramagnetic. The best fit parameters were $J=-48.2(3)$ and $J'=-11.2(3)$ cm^{-1} for $\mathcal{H}=-2J(S_1\cdot S_{1'})-2J'(S_1\cdot S_2)$.

Chemistry of metal complexes with cyclam or related tetraazamacrocyclic ligands has been extensively developed.[1] Dinucleating ligands with two such macrocyclic rings were also prepared, aiming at the cooperative interactions of the two metallic sites in metal complexes.[2] We prepared a new dinucleating ligand (L) comprised of two dimethylcyclams bridged at the carbon with *ortho*-xylylene group,[3,4] and have been studying chemistry of its dinuclear complexes of various metal ions (Chart 1). In the previous communication, we reported the synthesis of the dinucleating ligand (L) and its nickel(II) and zinc(II) complexes, $[Ni_2(\mu\text{-Br})Br_2(L)]Br\cdot H_2O$ and $[Zn_2(\mu\text{-}CO_3)(L)](ClO_4)_2\cdot 1.5H_2O$.[3] Two cyclam rings in these complexes are arranged in a face-to-face manner where effective use of the bimetallic site is highly probable. It has been shown that the presence of two methyl groups on each cyclam ring skeleton brought about the cofacial ring arrangement. The metal–metal separations were 5.802(2) Å in the Br^- bridged nickel complex and 5.806(2) Å in the $CO_3{}^{2-}$ bridged zinc complex. The carbonatodizinc(II) complex has been obtained by the spontaneous CO_2 uptake from the air by $[Zn_2L]^{4+}$.

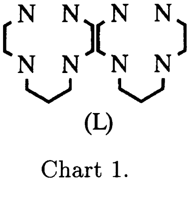
(L)

Chart 1.

The linear Br–Ni–Br–Ni–Br structure in $[Ni_2(\mu\text{-Br})Br_2(L)]Br\cdot H_2O$, which arises from the face-to-face cyclam ring arrangement, suggests that this type of complex can be a potential building block for making halogen–Ni(II) alternate chain structure. Such nickel(II) complexes with the one dimensional and antiferromagnetically coupled chain structure are known as Haldaine complex and deeply investigated.[5] In this paper, we report a nickel(II) complex with this dinucleating ligand (L) in which nickel(II) and chloride ions are alternately arranged to form a linear chain-like structure. A repeating unit of the chain is a unique nickel(II) tetramer. Magnetic interactions between nickel ions are also described.

Experimental

Materials. α,α'-Bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecan-6-yl)-*o*-xylene (L) and $[Ni_2(\mu\text{-Br})Br_2(L)]Br\cdot H_2O$ were prepared as reported previously.[3]

Preparation of $Ni_2Cl_2(L)(ClO_4)_2\cdot 1.5H_2O$. Recrystallization of $[Ni_2(\mu\text{-Br})Br_2(L)]Br\cdot H_2O$ from 1 M sodium perchlorate aqueous solution gave yellow microcrystalline needles of $[Ni_2(L)](ClO_4)_4\cdot 4H_2O$ (M = mol dm^{-3}, Anal. Calcd for $C_{32}H_{70}N_8O_{20}Cl_4Ni_2$: C, 33.53; H, 6.16; N, 9.78%. Found: C, 33.43; H, 5.47; N, 9.71%). $[Ni_2(L)](ClO_4)_4\cdot 3H_2O$ was dissolved in a 1 M NaCl hot aqueous solution and cooled down slowly to the room temperature. Resulting purple blocks were filtered off and dried in vacuo. Anal. Calcd for $C_{32}H_{65}N_8O_{9.5}Cl_4Ni_2$ ($=Ni_2Cl_2(L)(ClO_4)_2\cdot 1.5H_2O$): C, 39.50; H, 6.73; N, 11.51; Cl, 14.57%. Found: C, 39.75; H, 6.72; N, 11.64; Cl, 14.24%.

Crystallography. A purple block of $Ni_2Cl_2(L)(ClO_4)_2\cdot 1.5H_2O$ with dimensions of 0.49×0.33×0.30 mm^3 was sealed in glass capillary and used for data collection. Diffraction experiments were performed on an Enraf–Nonius

CAD4 automated diffractometer using graphite-monochromatized Cu $K\alpha$ radiation (λ=1.5418 Å). The intensity measurement was carried out at −80 °C. The orientation matrix and the lattice parameters were determined from 25 machine-centered high-angle reflections (26.0°< 2θ <36.2°). Three standard reflections were recorded every 2 h and their intensities showed no statistically significant change over the duration of data collection. Intensities were corrected for Lorentz and polarization effects and for absorption. The structure was solved using the direct method, SHELX-86,[6] and successive Fourier syntheses (XTAL 3.2).[7] Intermolecularly bridged Cl(3) atom was found to be disordered and was located at two positions related by crystallographic mirror plane with an occupation factor of 0.5 (vide infra). The structure was refined finally on F by full-matrix least squares method (XTAL 3.2). All the non-hydrogen atoms were refined anisotropically while all hydrogen atoms isotropically, giving the final R value of 0.065. The crystallographic data are summarized in Table 1. Tables of crystallographic data, experimental conditions, full atomic positional and thermal parameters, interatomic distances and bond angles, and observed and calculated structure factors have been deposited as Document No. 67045 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Magnetic Susceptibility Measurement. Powder susceptibility measurements were performed using a Quantum Design Model MPMS SQUID magnetometer over the temperature range 2—300 K. The independence of the magnetic susceptibility versus the applied field was checked at room temperature. The X-ray analysis shows that this compound is a tetrameric nickel(II) complex and is formulated to be $\{Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O\}_2$ (vide infra). The molar susceptibility calculated for the tetramer was corrected for diamagnetism (-1152.686×10^{-6} emu mol^{-1}) and the temperature-independent paramagnetism (300×10^{-6} emu mol^{-1}) was included in the calculation.

Results and Discussion

Synthesis. The present compound $Ni_2Cl_2(L)$-

Table 1. Crystallographic Data for $[Ni_2Cl_2(L)](ClO_4)_2 \cdot 1.5H_2O$

Empirical formula	$C_{32}H_{65}N_8Ni_4Cl_4O_{9.5}$
Formula weight	973.13
Space group	$Ccm2_1$(#36)
a/Å	21.90(1)
b/Å	20.28(1)
c/Å	19.63(1)
V/Å^3	8718(1)
Z	8
D_{calcd}/g cm^{-3}	1.48
μ(Cu $K\alpha$)/cm^{-1}	49.17
Radiation (Cu $K\alpha$)/Å	1.5418
Temperature/°C	−80
No. of data	5042
No. of data with I>3.00$\sigma(I)$	3494
$R^{a)}$	0.065
$R_w{}^{b)}$	0.088

a) $R=\sum(|F_o|-|F_c|)/\sum|F_o|$. b) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w=1/\sigma^2(F_o)$.

Table 2. Positional and Thermal Parameters

Atom	x/a	y/b	z/c	U(eq)$^{a)}$/Å^2
Ni(1)	0.62138(6)	0.60579(7)	0.31477(8)	0.0359(4)
Ni(2)	0.86633(7)	0.62672(7)	0.28147(9)	0.0426(4)
N(3)	0.6074(3)	0.6864(3)	0.2571(4)	0.023(2)
N(4)	0.6315(3)	0.6704(3)	0.3938(4)	0.021(2)
N(5)	0.6286(3)	0.5227(3)	0.3745(3)	0.021(2)
N(6)	0.6094(3)	0.5425(4)	0.2355(4)	0.026(2)
N(7)	0.8627(3)	0.7112(4)	0.3343(4)	0.028(2)
N(8)	0.8697(4)	0.5685(4)	0.3638(4)	0.030(2)
N(9)	0.8606(4)	0.6819(5)	0.1988(4)	0.035(3)
N(10)	0.8743(4)	0.5436(4)	0.2278(4)	0.035(3)
C(1)	0.8773(4)	0.6624(5)	0.4475(5)	0.028(3)
C(2)	0.8073(4)	0.6696(5)	0.4623(5)	0.030(3)
C(3)	0.7854(4)	0.6472(5)	0.5314(5)	0.029(3)
C(4)	0.8133(5)	0.6738(5)	0.5900(5)	0.037(3)
C(5)	0.7963(5)	0.6575(5)	0.6556(5)	0.036(3)
C(6)	0.7475(5)	0.6157(5)	0.6649(5)	0.033(3)
C(7)	0.7190(4)	0.5904(5)	0.6084(5)	0.030(3)
C(8)	0.7358(4)	0.6050(4)	0.5249(4)	0.022(2)
C(9)	0.7020(4)	0.5722(5)	0.4852(5)	0.030(3)
C(10)	0.6312(4)	0.5824(5)	0.4842(5)	0.024(3)
C(11)	0.9011(4)	0.7120(5)	0.3968(5)	0.030(3)
C(12)	0.8772(5)	0.7650(5)	0.2831(6)	0.041(3)
C(13)	0.8444(6)	0.7493(6)	0.2201(6)	0.047(4)
C(14)	0.8209(5)	0.6576(6)	0.1415(5)	0.044(4)
C(15)	0.8430(6)	0.5895(7)	0.1149(6)	0.055(5)
C(16)	0.8358(5)	0.5363(6)	0.1659(6)	0.045(4)
C(17)	0.8670(5)	0.4891(5)	0.2743(7)	0.050(4)
C(18)	0.8954(6)	0.5054(5)	0.3403(6)	0.043(4)
C(19)	0.8972(5)	0.5908(5)	0.4293(5)	0.034(3)
C(20)	0.9047(5)	0.7806(5)	0.4288(6)	0.042(4)
C(21)	0.8892(7)	0.5414(6)	0.4890(7)	0.060(5)
C(22)	0.6002(4)	0.5288(4)	0.4418(4)	0.022(3)
C(23)	0.6075(4)	0.4676(4)	0.3313(5)	0.027(3)
C(24)	0.6321(4)	0.4779(5)	0.2597(5)	0.031(3)
C(25)	0.6332(5)	0.5612(5)	0.1696(5)	0.037(3)
C(26)	0.6085(5)	0.6281(5)	0.1459(5)	0.035(3)
C(27)	0.6302(5)	0.6864(5)	0.1859(5)	0.033(3)
C(28)	0.6272(5)	0.7439(5)	0.2966(5)	0.030(3)
C(29)	0.6050(5)	0.7348(5)	0.3702(5)	0.033(3)
C(30)	0.6107(5)	0.6527(5)	0.4625(4)	0.026(3)
C(31)	0.5961(5)	0.4645(5)	0.4815(5)	0.033(3)
C(32)	0.6241(5)	0.7046(5)	0.5170(5)	0.035(3)
Cl(1)	1/2	0.6051(2)	0.3245(2)	0.0282(9)
Cl(2)	0.7373(1)	0.6129(1)	0.2961(1)	0.0408(8)
Cl(3)$^{b)}$	0.9840(2)	0.6335(2)	0.2764(3)	0.037(2)
Cl(4)	0.7649(1)	0.3741(2)	0.4084(2)	0.060(1)
Cl(5)	1/2	0.5976(2)	0.6501(3)	0.050(1)
Cl(6)	1/2	0.8149(4)	0.1410(5)	0.113(3)
O(41)	0.8287(5)	0.3741(5)	0.424(1)	0.120(7)
O(42)	0.7511(6)	0.3188(7)	0.3715(8)	0.137(7)
O(43)	0.7466(6)	0.4337(6)	0.3813(7)	0.111(5)
O(44)	0.7339(6)	0.3660(6)	0.4744(7)	0.105(6)
O(51)	1/2	0.5387(7)	0.686(1)	0.105(8)
O(52)	0.5541(5)	0.6329(6)	0.6580(6)	0.096(5)
O(53)	1/2	0.581(1)	0.580(1)	0.13(1)
O(61)	1/2	0.7723(9)	0.199(1)	0.109(8)
O(62)	0.5522(5)	0.8566(7)	0.148(1)	0.20(1)
O(63)	1/2	0.784(2)	0.085(3)	0.33(3)
O(31)	1	0.7183(6)	0.146(1)	0.090(7)
O(32)	1	0.505(1)	0.1597(9)	0.094(7)
O(33)	1	0.6055(8)	0.061(1)	0.115(9)

a) Equivalent isotropic U defined as one-third of the trace of the orthogonallized U_{ij} tensor. b) Occupation factor=0.5.

$(ClO_4)_2\cdot1.5H_2O$ was prepared via a four coordinate complex $[Ni_2(L)](ClO_4)_4\cdot3H_2O$ from $[Ni_2(\mu\text{-}Br)Br_2(L)]Br\cdot H_2O$, which is a good starting material to compounds with the $\{Ni_2(L)\}$ moiety as described previously.3) The compound $Ni_2Cl_2(L)(ClO_4)_2\cdot1.5H_2O$ precipitates out as purple block crystals from yellow 1 M NaCl aqueous solution of $[Ni_2(L)](ClO_4)_4\cdot3H_2O$. The yellow color of the solution suggests that the species in the solution exists as square-plannar four coordinate complex. Slow recrystallization of $[Ni_2(L)](ClO_4)_4\cdot3H_2O$ from 1 M NaBr aqueous solution yielded similarly purple powdery product of the bromo analog, but crystals suitable for X-ray work were not obtained.

Molecular Structure. Table 2 lists positional and thermal parameters for the non-hydrogen atoms in $Ni_2Cl_2(L)(ClO_4)_2\cdot1.5H_2O$. Selected bond distances and angles are given in Table 3 and Table 4. The crystal consists of the cationic dinuclear unit $[Ni_2Cl_3(L)]^+$, the counter anion ClO_4^-, and water of crystallization. Figure 1 shows the structure of $[Ni_2Cl_3(L)]^+$ with the atomic numbering scheme. A linear chain structure is shown in Fig. 2. The Cl(3) atom was disordered at two positions (Cl(3) and Cl(3″)) related by crystallographic mirror plane with an occupation factor of 0.5 (see Fig. 2). As shown in Fig. 1, the cationic unit is a dinuclear Ni(II) complex formed with the dinucleating ligand (L) and three Cl^- ions. Two dimethylcyclam rings are arranged in a face-to-face manner. Three chloride ions and two nickel ions are alternately arranged in an almost linear way (see Table 4) and Cl(2) bridges between Ni(1) and Ni(2). The overall structural feature is very similar to that of $[Ni_2(\mu\text{-}Br)Br_2(L)]^+$.3) Ni(1) and Ni(2) sit in the hole of cyclam ring and deviation of nickel atom from the plane defined by four nitrogen donors is less than 0.05 Å (0.049(2) Å for Ni(1) and 0.011(2) Å for Ni(2)). Each cyclam ring skelton takes the most stable "*trans*-III" conformation.8) The arrangement of chloride ions are not simple. Cl(2) is not located around the center of Ni(1) and Ni(2) but is situated in closer proximity to Ni(1). The Ni(1)–Cl(2) distance is 2.568(4) Å, whereas Ni(2)–Cl(2) separation is 2.855(4) Å which is beyond the values normally found for the Ni(II)–Cl coordination bonds. The Ni–Cl distance in *trans*-$[NiCl_2(cyclam)]$ has been reported to be 2.492(3) Å.9) However, the Ni(2)–Cl(2) separation of 2.855(4) Å is shorter than the sum of Van der Waals radii (1.75 Å for Cl and 1.63 Å for Ni)10) and may be indicative of weak interaction between them (vide infra). Such an unsymmetrical arrangement of Cl(2) may arise from the fact that chloride ion is too small to form a symmetrically bridged Ni(II) dimer with the present dinucleating ligand (L). The Ni(1)–Cl(1) bond (2.665(2) Å) is slightly longer but can be taken as a coordination bond. Thus the coordination geometry around Ni(1) is of the tetragonally distorted octahedral type. The coordinaiton geometry around Ni(2) is rather complicated. In addition to the long Ni(2)–Cl(2) separation (2.855(4) Å), the Cl(3) atom is disordered

Table 3. Selected Bond Distances and Interatomic Distances (Å)

Ni(1)–Cl(1)	2.665(2)	Ni(2)–Cl(2)	2.855(4)
Ni(1)–Cl(2)	2.568(4)	Ni(2)–Cl(3)	2.582(5)
Ni(1)–N(3)	2.012(7)	Ni(2)–N(7)	2.004(8)
Ni(1)–N(4)	2.042(7)	Ni(2)–N(8)	2.003(8)
Ni(1)–N(5)	2.058(7)	Ni(2)–N(9)	1.976(9)
Ni(1)–N(6)	2.035(8)	Ni(2)–N(10)	1.996(9)
Ni(2)–Cl(3″)	3.283(5)	Cl(3)–Cl(3″)	0.702(6)
Ni(1)–Ni(2)	5.421(3)	Ni(1)–Ni(1′)	5.317(3)
Ni(2)–Ni(2″)	5.855(3)		

Table 4. Selected Bond Angles (deg)

Cl(1)–Ni(1)–Cl(2)	174.9(1)	Cl(2)–Ni(2)–Cl(3)	175.6(1)
Ni(1)–Cl(1)–Ni(1′)	171.8(2)	Ni(1)–Cl(2)–Ni(2)	176.5(1)
Cl(1)–Ni(1)–N(3)	83.8(2)	Cl(2)–Ni(2)–N(7)	89.6(2)
Cl(1)–Ni(1)–N(4)	93.3(2)	Cl(2)–Ni(2)–N(8)	84.1(2)
Cl(1)–Ni(1)–N(5)	91.8(2)	Cl(2)–Ni(2)–N(9)	94.3(2)
Cl(1)–Ni(1)–N(6)	85.6(2)	Cl(2)–Ni(2)–N(10)	93.2(2)
Cl(2)–Ni(1)–N(3)	91.4(2)	Cl(3)–Ni(2)–N(7)	90.8(3)
Cl(2)–Ni(1)–N(4)	88.1(2)	Cl(3)–Ni(2)–N(8)	91.5(3)
Cl(2)–Ni(1)–N(5)	92.9(2)	Cl(3)–Ni(2)–N(9)	90.1(3)
Cl(2)–Ni(1)–N(6)	93.0(2)	Cl(3)–Ni(2)–N(10)	86.4(3)
N(3)–Ni(1)–N(4)	85.6(3)	N(7)–Ni(2)–N(8)	95.0(3)
N(3)–Ni(1)–N(5)	175.6(3)	N(7)–Ni(2)–N(9)	86.5(3)
N(3)–Ni(1)–N(6)	93.6(3)	N(7)–Ni(2)–N(10)	177.1(3)
N(4)–Ni(1)–N(5)	94.9(3)	N(8)–Ni(2)–N(9)	177.8(3)
N(4)–Ni(1)–N(6)	178.6(3)	N(8)–Ni(2)–N(10)	85.7(3)
N(5)–Ni(1)–N(6)	85.9(3)	N(9)–Ni(2)–N(10)	92.9(4)

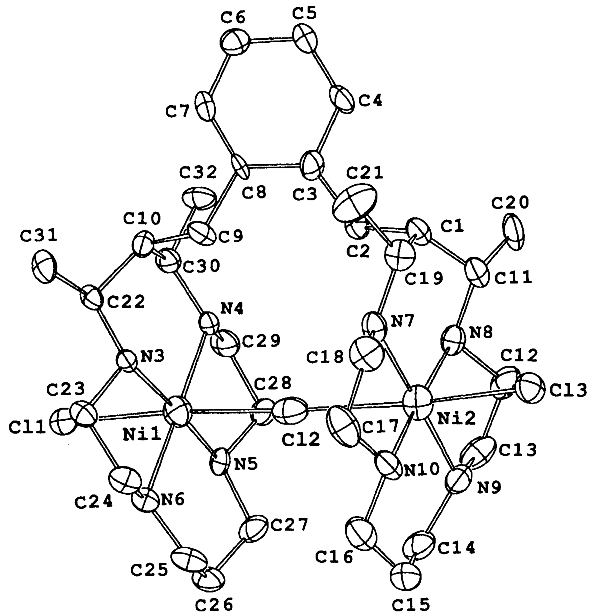

Fig. 1. ORTEP drawing of the cation part in $Ni_2Cl_2(L)(ClO_4)_2\cdot1.5H_2O$. The thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity.

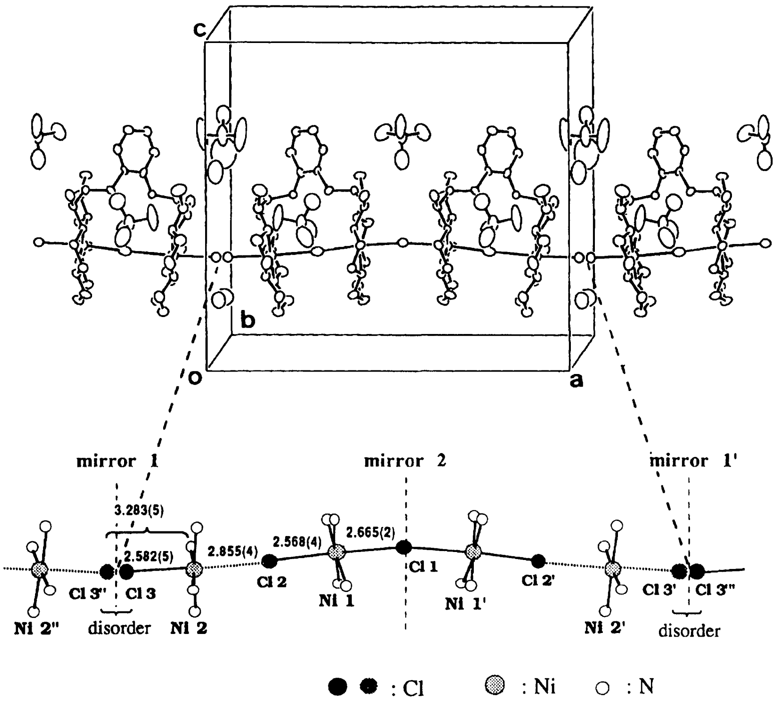

Fig. 2. The arrangement of $Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O$ in the lattice. For clarity, only two asymmetric units along the chain are depicted in a cell. The drawing underneath shows schematically the Ni–Cl alternate chain along with interatomic distances (Å).

at two positions (Cl(3) and Cl(3″)), which are 0.702(6) Å apart from each other. The Ni(2)–Cl(3) and Ni(2)–Cl(3″) separations are 2.582(5) and 3.283(5) Å, respectively, latter of which is again beyond the normal coordination bond distance. Accordingly, the coordination geometry about Ni(2) should be taken as the square-planar 4-coordinate type at 50% probability and the square-pyramidal 5-coordinate type at 50% probability. The difference in the chloride ion coordination between Ni(1) and Ni(2) is reflected in Ni–N distances. Ni–N distances around Ni(1) with the coordination number 6 are slightly longer (2.012(7)—2.058(7) Å) than those around Ni(2) with the lower coordination number (1.976(9)—2.004(8) Å). A similar phenomenon is often observed in complexes of the *trans*-MX_2N_4 type and is called "*cis*-effect" or "axial-equatorial interaction".[11] A Ni–Ni separation within the dinuclear unit (Ni(1)–Ni(2)=5.421(3) Å) is significantly shorter than Ni–Ni distance in $[Ni_2(\mu\text{-}Br)Br_2(L)]^+$ (5.802(2) Å).[3]

In the crystal structure, a pseudo one-dimensional linear arrangement of ···Cl–Ni–Cl–Ni–Cl··· is formed along the *a* axis (Fig. 2). There are two crystallographic mirror planes perpendicular to the *a* axis, which are depicted in Fig. 2 as mirror plane (1) at $x=0$ and mirror plane(2) at $x=0.5$. Atoms related by the mirrors are labeled with prime(s). The Cl(1) atom is situated on the mirror(2) and acts as an intermolecular bridge between Ni(1) and Ni(1′) with the Ni(1)–Cl(1) distance of 2.665 (2) Å and the Ni(1)–Ni(1′) separation of 5.317(3) Å. On the other hand, the Ni(2)–Ni(2′) separation is 5.855(3) Å. The bond distance parameters along the chain show that the repeating unit of the chain is considered to be a tetrameric Ni(II) complex, that is, a chloro-bridged dimer of the dinucleating ligand complex. The chain deviates slightly from a straight line. The largest bent occurs at Cl(1) with the Ni(1)–Cl(1)–Ni(1′) angle of 171.8(2)°. No special close contact was observed between the cationic chains.

UV-vis Spectra. UV-vis spectrum of $Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O$ in aqueous solution shows an absorption maximum (λ_{max}) at 452 nm ($\varepsilon_{max}=82$ cm M^{-1}) with very weak maxima at 340 nm (25) and at 660 nm (9). The spectral pattern is identical with those of $[Ni_2(L)](ClO_4)_4 \cdot 3H_2O$ ($\lambda_{max}=340$ nm ($\varepsilon_{max}=33$), 456 (64), and 660 (12)) and *trans*-$[NiCl_2(cyclam)]$ ($\lambda_{max}=456$ (49))[9] in aqueous solution. It has been shown that *trans*-$[NiCl_2(cyclam)]$ exists predominantly as square-planar four coordinate species in aqueous solution, and therefore the chloro ligands in $Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O$ dissociate completely in aqueous solution to give a mutually independent dimer of the four coordinate Ni(II) complex, $[Ni_2(L)]^{4+}$.

On the other hand, the single crystal transmission spectrum of $Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O$ is different from that in the solution state and shows a broad peak at 480 nm and a moderately intense shoulder around 660 nm. The spectrum is too broad to discuss in detail but it appears to reflect the three coordination geometries around Ni(II) in the solid state (vide ante).

Magnetic Property. Figure 3 shows a plot of the product of molar susceptibility and temperature ($\chi_M T$) vs. temperature. The value of χ_M was calculated for the

Table 5. Eigenvalues for Seven Spin-States That Arise from Magnetic Interaction among Three High Spin Nickel(II) Ions

Total spin	Eigenvalue
$S_T=3$	$E_3=-2(J+J')$
$S_T=2\Bigg\{$	$E_2^a=-2\sqrt{J^2+J'^2-JJ'}$
	$E_2^b=2\sqrt{J^2+J'^2-JJ'}$
$S_T=1$	$E_1^k=\frac{2}{3}\sqrt{7(J_+^2+3J_-^2)}\cos\left(\frac{1}{3}\left[\arccos\frac{-10(9J_+J_-^2-3J_+^3)}{\sqrt{[7(J_+^2+3J_-^2)]^3}}+120°k\right]\right)+\frac{4}{3}J_+$
	where $k=0,1$, and 2, $J_+=J+J'$ and $J_-=J-J'$
$S_T=0$	$E_0=2(J+J')$

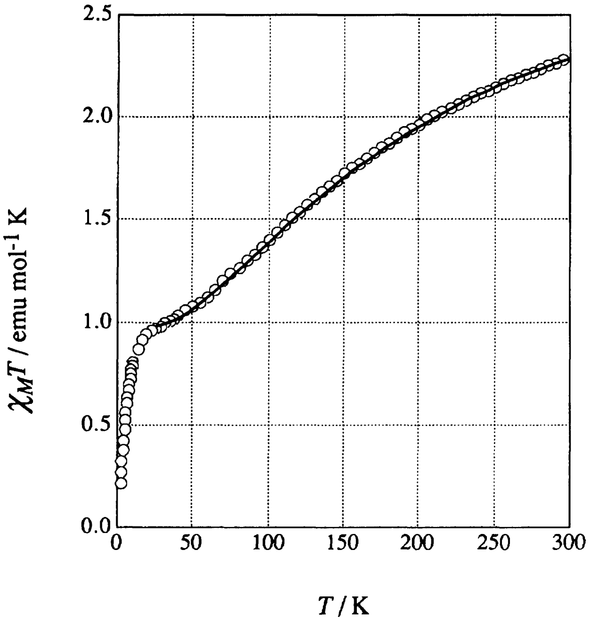

Fig. 3. Plot of $\chi_M T$ vs. T for $\{Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O\}_2$. Experimental data are shown as circles and the best fit to the tetramer expression (see text) is displayed as a solid line.

Ni-tetramer, $\{Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O\}_2$. $\chi_M T$ decreases slowly as the temperature decreases, and reaches to an approximately constant value of 1.0 emu mol^{-1} K at the range of 50—20 K. Then it rapidly decreases at lower temperature. The $\chi_M T$ behavior indicated antiferromagnetic interactions among nickel(II) ions. Structural characterization shows that Ni(1) and Ni(1′) are in the tetragonally distorted octahedral environment and thereby paramagnetic, and that Ni(2) and Ni(2′) are four-coordinate (diamagnetic) at 50% probability and five-coordinate (paramagnetic)[12] at 50% probability. We tried to explain semiquantitatively the overall magnetic behavior of this compound on the following assumption: (i) magnetic interaction between Ni(2) and Ni(2″) is negligibly small in view of the separation of 5.853(3) Å; (ii) on the average, three nickel ions, Ni(1), Ni(1′), and Ni(2) are paramagnetic.

We will discuss the magnetic susceptibility of $Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O$ in terms of the usual Heisenberg–Dirac–Van Vleck spin-coupling Hamiltonian where Hamiltonian is expressed as,

$$\mathscr{H} = -2J(\boldsymbol{S}_1 \cdot \boldsymbol{S}_{1'}) - 2J'(\boldsymbol{S}_1 \cdot \boldsymbol{S}_2).$$

J and J' are the exchange integrals between central Ni(1) and Ni(1′) and between Ni(1) and Ni(2), respectively. $\boldsymbol{S}_i$ is spin angular momentum operator. As Ni(2) and Cl(2) are far separated, the magnetic interaction between Ni(1) and Ni(2) must be much weaker than that between Ni(1) and Ni(1′), hence $|J'|$ should be smaller than $|J|$.

A tri-nuclear system with two unpaired spins on each metal atom has seven spin states. The general expressions of eigenvalues for the seven spin states were reported by Sinn.[13] We derived eigenvalues for all the arising spin-states according to the manner of Sinn. The eigenvalues for each spin states are given in Table 5 using J and J', where S_T is the total spin of the tetramer. The magnetic behavior of the complex is explained by the thermal distribution on the seven spin-states. The susceptibility data above 25 K were fitted by Van Vleck formula where the zero-field splitting for nickel(II) ions was not taken into account.[14] The result is shown in Fig. 3 as a solid line showing a reasonable agreement with observed values. Best fit parameters were $J=-48.2(3)$ cm^{-1}, $J'=-11.2(3)$ cm^{-1}, and $g=1.973(2)$.

There are two kinds of magnetic interactions, those between Ni(1) and Ni(2) (intra dimer) and between Ni(1) and Ni(1′) (inter dimer). Both are antiferromagnetically coupled and are the typical superexchange pathway model by Goodenough–Kanamori.[15] The interdimer interaction is strong, while the intradimer one is weak. As previously described, this is due to the different Ni–Cl distances (2.665(2) Å for Ni(1)–Cl(1) and 2.855(4) Å for Ni(2)–Cl(2)).

Conclusion. Our original purpose was to synthesize a compound with one-dimensional structure of the ···Cl–Ni–Cl–Ni–Cl··· type, using the Ni_2L dimer-units. We succeeded in making the linearly arranged chloro-bridged Ni(II) tetramer, that is, the chloro-bridged dimer of the dinucleating ligand complex. Although the linking of the inter Ni(II)-tetramer was incomplete because of occurrence of the disorder for the bridging Cl(3) atom, the chain-like structure was formed as a whole.

Replacement of the chloride ion to larger anion such as bromide or iodide ion may be one way to approach the complete one-dimensional alternate chain. The magnetic behavior of $Ni_2Cl_2(L)(ClO_4)_2 \cdot 1.5H_2O$ was semiquantitatively interpreted by the calculation for the tetramer.

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