Synthesis, Structures and Characterization of the Dinuclear Nickel(II) Complexes Containing *N*,*N*,*N′*,*N′*-Tetrakis[(1-ethyl-2-benzimidzolyl)-methyl]-2-hydroxy-1,3-diaminopropane and their Urea Complexes Relevant to the Urease Active Site

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New dinuclear nickel(II) complexes ([Ni_2(L-Et)(CH_2ClCOO)$(H_2O)_2$]$(ClO_4)_2$·H_2O (**3**), [Ni_2(L-Et)(CCl_3COO)$(H_2O)_2$]$(ClO_4)_2$·H_2O (**4**), [Ni_2(L-Et)(CF_3COO)$(H_2O)_2$]$(ClO_4)_2$·$3H_2O$ (**5**)) and their urea complexes ([Ni_2(L-Et)(RCOO)(ur)(H_2O)]$(ClO_4)_2$ (R = CH_3 (**6**), C_2H_5 (**7**), CH_2Cl (**8**), CCl_3 (**9**), CF_3 (**10**)) (HL-Et = *N*,*N*,*N′*,*N′*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane and ur = urea) have been prepared in order to model the active site urease. These complexes were characterized by IR and UV-vis spectra, and by magnetic susceptibilities. The crystal structures of the complexes [Ni_2(L-Et)(CH_2ClCOO)$(CH_3OH)_2$]$(ClO_4)_2$ (**3′**) and [Ni_2(L-Et)(OAc)(ur)(H_2O)]$(ClO_4)_2$·2$(CH_3)_2CO$ (OAc = acetate) (**6′**) were determined by X-ray crystallography. In the cation of **6′**, the two nickel(II) ions are bridged by an alkoxo of L-Et$^-$ and an acetato, and a monodentate urea molecule is attached to a nickel(II) through its oxygen atom. Variable temperature magnetic susceptibility measurements of the urea complexes **6**, **8**, and **10** show an antiferromagnetic exchange coupling ($2J = -15.8$, -8.0, and -13.3 cm^{-1} for **6**, **8**, and **10**, respectively, Hamiltonian $H = -2JS_1 \cdot S_2$ with $S_1 = S_2 = 1$) between two nickel(II) ions.

There is current interest in the structure and catalytic function of the active sites of nickel(II) containing metalloproteins.[1] The best known enzyme urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide. Recently, Jabri et al. reported the crystal structure of bacterial urease isolated from *Klebsiella aerogenes* (KAU), in which a carboxylate group of a carbamylated ε-amino residue of lysine-217 bridges two nickel(II) ions.[2] Although two nickel(II) ions are coordinated by two imidazole nitrogens of histidine residue, the coordination environments around each nickel(II) are non-equivalent to each other. One nickel(II) is in a three-coordination environment and the other nickel(II) is in a five-coordination bound additionally by the carboxylate oxygen of aspartate-360 and a water molecule. The Ni···Ni separation is 3.5 Å (1 Å = 1 × 10^{-10} m). In the most important step of the proposed mechanism of urea hydrolysis, a coordinated hydroxide ion for nickel(II) attacks nucleophilically the carbonyl carbon atom of the urea which is coordinated to the other nickel(II).[3,4] Very recently, the crystal structure from a bacterial source, *Bacillus pasteurii* (BPU) has been reported by Benini et al.[5] In BPU, the two nickel(II) ions are bridged by the carboxylate group of the carbamoylated lysine-220 and hydroxide. One of two nickel(II) ions has a five-coordinate distorted square pyramidal geometry, whereas the other nickel has a six-coordinate distorted octahedral geometry. The Ni···Ni separation is 3.7 Å.

In connection with these studies, some dinuclear nickel(II) complexes have been reported so far as models for the active site of urease.[6–20] To provide further analogues of the urease active site, we have synthesized five dinuclear nickel(II) complexes containing *N*,*N*,*N′*,*N′*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (HL-Et): [Ni_2(L-Et)(OAc)$(H_2O)_2$]$(ClO_4)_2$·H_2O (**1**) (OAc = acetate),[19,20] [Ni_2(L-Et)(C_2H_5COO)$(H_2O)_2$]$(ClO_4)_2$·H_2O (**2**),[19,20] [Ni_2(L-Et)(CH_2ClCOO)$(H_2O)_2$]$(ClO_4)_2$·H_2O (**3**), [Ni_2(L-Et)(CCl_3COO)$(H_2O)_2$]$(ClO_4)_2$·H_2O (**4**), and [Ni_2(L-Et)(CF_3COO)$(H_2O)_2$]$(ClO_4)_2$·$3H_2O$ (**5**). Further, we have synthesized their urea complexes: [Ni_2(L-Et)(OAc)(ur)(H_2O)]$(ClO_4)_2$ (**6**) (ur = urea), [Ni_2(L-Et)(C_2H_5COO)(ur)(H_2O)]$(ClO_4)_2$ (**7**), [Ni_2(L-Et)(CH_2ClCOO)(ur)(H_2O)]$(ClO_4)_2$·H_2O (**8**), [Ni_2(L-Et)(CCl_3COO)(ur)(H_2O)]$(ClO_4)_2$·1/2H_2O (**9**), and [Ni_2(L-Et)(CF_3COO)(ur)(H_2O)]$(ClO_4)_2$·H_2O (**10**) (Chart 1,structural formula I), and characterized them by magnetic susceptibilities, IR and UV-vis spectra with X-ray crystallographic analysis of [Ni_2(L-Et)(CH_2ClCOO)$(CH_3OH)_2$]$(ClO_4)_2$ (**3′**) and [Ni_2(L-Et)(OAc)-

(ur)(H_2O)](ClO_4)$_2$·2(CH_3)$_2$CO (**6′**) similar to **3** and **6**.

Experimental

Preparation of HL-Et. HL-Et was synthesized according to the method described in the literature.[21] **Caution!** Although no problems were encountered in this work, transition metal perchlorate complexes are potentially explosive and should be handled with proper precautions.

Preparation of Nickel(II) Complexes. [Ni_2(L-Et)(OAc)(H_2O)$_2$](ClO_4)$_2$·3H_2O, **1** and [Ni_2(L-Et)(C_2H_5COO)(H_2O)$_2$](ClO_4)$_2$·H_2O, **2**. These complexes were synthesized according to the method described in the literature.[19,20]

[Ni_2(L-Et)(CH_2ClCOO)(H_2O)$_2$](ClO_4)$_2$·H_2O, 3 and [Ni_2(L-Et)(CH_2ClCOO)(CH_3OH)$_2$](ClO_4)$_2$, 3′. To an ethanol solution (20 cm^3) of nickel(II) perchlorate hexahydrate (1.10 g, 3.0 mmol) were added successively HL-Et (1.09 g, 1.5 mmol), sodium hydroxide (0.06 g, 1.5 mmol) and chloroacetic acid (0.14 g, 1.5 mmol). The reaction mixture was stirred at room temperature for 1 d and then allowed to stand for several hours at 5 °C. After it had been filtered, a crude complex was recrystallized from methanol. The crystal of **3′** is stable in methanol solution. The complex **3′**, however, readily turns to **3** by filtration. Anal for **3**. Found: C, 45.60; H, 4.67; N, 11.96; Ni, 10.30%. Calcd for $C_{45}H_{55}N_{10}O_{13}Cl_3Ni_2 \cdot H_2O$: C, 45.57; H, 4.85; N, 11.81; Ni, 9.90%.

[Ni_2(L-Et)(CCl_3COO)(H_2O)$_2$](ClO_4)$_2$·H_2O, 4. This complex was prepared in the same way as **3** using trichloroacetic acid (0.25 g, 1.5 mmol) instead of chloroacetic acid, and recrystallized from methanol. Found: C, 43.23; H, 4.28; N, 11.28; Ni, 8.82%. Calcd for $C_{45}H_{53}N_{10}O_{13}Cl_5Ni_2 \cdot H_2O$: C, 43.07; H, 4.43; N, 11.17; Ni, 9.36%.

[Ni_2(L-Et)(CF_3COO)(H_2O)$_2$](ClO_4)$_2$·3H_2O, 5. This complex was prepared in the same way as **3** using sodium trifluoroacetate (0.21 g, 1.5 mmol) instead of chloroacetic acid, and recrystallized from methanol. Found: C, 43.12; H, 4.73; N, 11.33; Ni, 9.60%. Calcd for $C_{45}H_{53}N_{10}O_{13}Cl_2F_3Ni_2 \cdot 3H_2O$: C, 43.53; H, 4.80; N, 11.29; Ni, 9.46%.

[Ni_2(L-Et)(OAc)(ur)(H_2O)](ClO_4)$_2$, 6 and [Ni_2(L-Et)(OAc)(ur)(H_2O)](ClO_4)$_2$·2(CH_3)$_2$CO, 6′. To an acetone solution (450 cm^3) of **1** (0.28 g, 0.25 mmol) was added urea (0.030 g, 0.50 mmol) and the mixture was stirred at room temperature for several hours, and then the resulting solution was concentrated under vacuum until the volume became to about 15 cm^3. Vapor diffusion of ether into obtainable solution gave light green crystals of **6′**. The crystal of **6′** is stable in acetone-ether solution. **6′** turns to **6** by filtration. Anal. of **6**. Found: C, 47.06; H, 4.87; N, 13.98; Ni, 10.22%. Calcd for $C_{46}H_{58}N_{12}O_{13}Cl_2Ni_2$: C, 47.00; H, 4.98; N, 14.30; Ni, 9.99%. IR (KBr) 1678 (C=O for urea), 1582 cm^{-1} (COO^-).

[Ni_2(L-Et)(C_2H_5COO)(ur)(H_2O)](ClO_4)$_2$, 7. This complex was obtained in the same way as **6** using **2** instead of **1**. Found: C, 47.89; H, 5.15; N, 14.05; Ni, 9.24%. Calcd for $C_{47}H_{60}N_{12}O_{13}Cl_2Ni_2$: C, 47.46; H, 5.09; N, 14.13; Ni, 9.87%. IR (KBr) 1664 (C=O for urea), 1572 cm^{-1} (COO^-).

[Ni_2(L-Et)(CH_2ClCOO)(ur)(H_2O)](ClO_4)$_2$·H_2O, 8. This complex was prepared in the same way as **6** using **3** instead of **1**. Found: C, 44.52; H, 4.93; N, 13.47; Ni, 9.74%. Calcd for $C_{46}H_{57}N_{12}O_{13}Cl_3Ni_2 \cdot H_2O$: C, 44.99; H, 4.85; N, 13.69; Ni, 9.56%. IR (KBr) 1667 (C=O for urea), 1609 cm^{-1} (COO^-).

[Ni_2(L-Et)(CCl_3COO)(ur)(H_2O)](ClO_4)$_2$·1/2H_2O, 9. This complex was prepared in the same way as **6** using **4** instead of **1**. Found: C, 42.61; H, 4.32; N, 12.89; Ni, 9.02%. Calcd for $C_{46}H_{55}N_{12}O_{13}Cl_5Ni_2 \cdot 1/2H_2O$: C, 42.90; H, 4.39; N, 13.06; Ni, 9.11%. IR (KBr) 1654 (C=O for urea), 1677 cm^{-1} (COO^-).

[Ni_2(L-Et)(CF_3COO)(ur)(H_2O)](ClO_4)$_2$·H_2O, 10. This complex was prepared in the same way as **6** using **5** instead of **1**. Found: C, 44.59; H, 4.63; N, 13.34; Ni, 9.44%. Calcd for $C_{46}H_{55}N_{12}O_{13}Cl_2F_3Ni_2 \cdot H_2O$: C, 44.29; H, 4.62; N, 13.48; Ni, 9.41%. IR (KBr) 1667 (C=O for urea), 1683 cm^{-1} (COO^-).

X-ray Structure Determination. Crystal structure analyses were carried out only for **3′** and **6′** because of the low quality of the crystals of the other complexes. X-ray diffraction data were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-*Kα* at room temperature. As the crystals **3′** and **6′** were unstable in the absence of solvents, the crystals were sealed in a capillary tube for the data collection. Lorenz, polarization and absorption effects were corrected for two crystals. The crystal structures were solved by direct method[22] and expanded using Fourier techniques.[23] The nonhydrogen atoms were refined anisotropically by the full-matrix least-squares techniques. The hydrogen atoms were fixed at their standard positions and were not refined. All calculations were performed by the use of teXsan crystallographic software package.[24] The crystallographic data and the experimental details for X-ray structure analyses are given in Table 1. The detail of structures have been deposited as Document No. 74057 at Office of the Editor of Bull. Chem. Soc. Jpn.

Measurements. IR and visible absorption spectra, and magnetic susceptibilities were carried out by the method reported previously.[25]

Results and Discussion

Synthesis and Structures of the Dinuclear Nickel(II) Complexes Bridged by Chloroacetate, Trichloroacetate, and Trifluoroacetate. The dinuclear nickel(II) complexes [Ni_2(L-Et)(OAc)(H_2O)$_2$](ClO_4)$_2$·3H_2O, **1** and [Ni_2(L-Et)(C_2H_5COO)(H_2O)$_2$](ClO_4)$_2$·H_2O, **2** containing L-Et$^-$ and an acetate or propionate ion had already been prepared and characterized.[19,20] Also, the complexes [Ni_2(L-Et)(OAc)(CH_3OH)$_2$](ClO_4)$_2$·CH_3OH·H_2O, **1′** and [Ni_2(L-Et)(C_2H_5COO)(CH_3OH)$_2$](ClO_4)$_2$· 2H_2O, **2′** similar to **1** and **2** were isolated and their structures were determined by X-ray methods. In order to elucidate the structure-catalytic function relationship of some dinuclear nickel(II) complexes, the dinuclear complexes **3**, **4**, and **5** bridged by chloroacetate, trichloroacetate or trifluoroacetate were prepared here in the same way as **1** and **2**. Each IR spectrum of **3**, **4**, and **5** shows the strong band of a carboxylate ligand at 1609, 1676, and 1682 cm^{-1} (ν_{as} (COO)), respectively. Electronic absorption spectra for these complexes in solid states exhibit three spin-allowed ligand-field bands (Table 2). From these IR and UV-vis spectra, and from elemental analysis, we suggest that compounds **3**, **4**, and **5** are dinuclear complexes bridged by one carboxylato and one alkoxo having the structures represented as I, which are similar to the structures **1** and **2**.[19,20] This was confirmed by the X-ray crystallography of **3′** as described below.

The Crystal and Molecular Structure of [Ni_2(L-Et)(CH_2ClCOO)(CH_3OH)$_2$](ClO_4)$_2$, 3′. The structure of the complex cation and the atom labelling scheme are shown in Fig. 1. Selected bond lengths and angles are given in Table 3. Each nickel center has an octahedral geometry with an N_3O_3 donor set from a bridging chloroacetato, an alkoxo of L-Et$^-$, a

Table 1. Crystal Data and Experimental Conditions for X-ray Analyses for **3′** and **6′**

Compound	**3′**	**6′**
Formula	$C_{47}H_{57}N_{10}O_{13}Cl_3Ni_2$	$C_{52}H_{70}N_{12}O_{15}Cl_2Ni_2$
Mol wt	1193.79	1291.50
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	16.044(6)	16.6403(2)
b/Å	16.749(8)	16.7598(3)
c/Å	12.728(2)	12.7778(4)
α/°	101.21(4)	104.036(2)
β/°	99.68(3)	102.704(2)
γ/°	64.45(3)	63.292(3)
V/Å^3	3013.0(21)	3062.9(1)
Z	2	2
D_c/g cm^{-3}	1.316	1.400
Radiation	Mo$K\alpha$	Mo$K\alpha$
λ/Å	0.7107	0.7107
μ/cm^{-1}	8.21	7.74
No. total reflections measured	6706	25998
No. observations	6567 ($I > 2.00\sigma(I)$)	7552 ($I > 2.00\sigma(I)$)
No. variables	676	748
F(000)	1240	1352
R	0.099	0.099
R_w	0.141	0.161

Table 2. Physical Properties of the Complexes **1**–**10**

Complex	ν/cm^{-1}		$\mu_{eff}$$^{a)}$	$\lambda_{max}$$^{c)}$
	COO	C=O(urea)	BM$^{b)}$	nm
1	1570$^{d)}$		2.94$^{d)}$	1039, 628, 396
2	1570$^{d)}$		3.15$^{d)}$	982, 655, 402
3	1609		3.15	987, 662, 401
4	1676		3.37	1014, 704, 411
5	1682		3.07	1023, 629, 382
6	1582	1678	3.19	1013, 639, 391
7	1572	1664	2.95	1021, 633, 387
8	1610	1667	3.14	1002, 640, 393
9	1667	1654	3.21	984, 655, 393
10	1683	1667	2.94	991, 622, 379

a) Room temperature. b) Non-S. I. units employed: BM = 9.27 JT^{-1}. c) Solid state. d) Ref. 20.

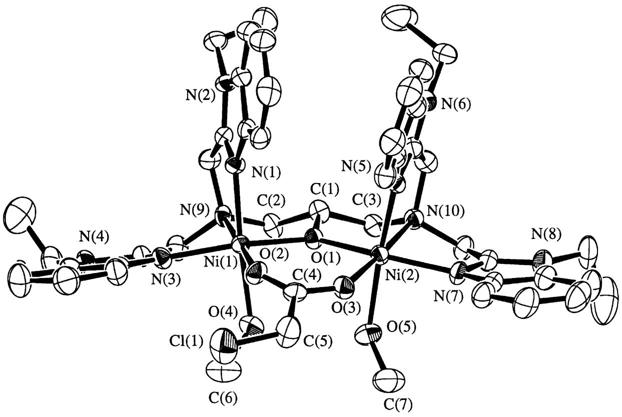


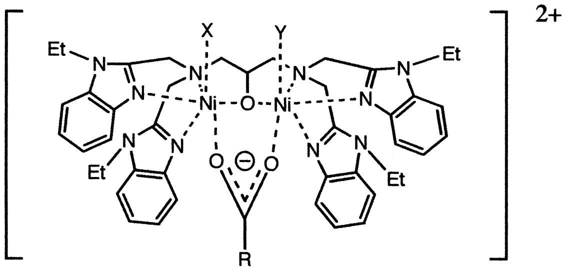
Fig. 1. An ORTEP drawing of [Ni_2(L-Et(CH_2ClCOO)(CH_3OH)$_2$]$^{2+}$ of **3′** with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

methanol molecule, a tertiary amino nitrogen and two imidazolyl nitrogens of L-Et$^-$. The alkoxo oxygen atom O(1) bridges the corner of the two octahedrons. The Ni(1)–O(1)–Ni(2) angle is 129.0(3)°, which is slightly larger than the corresponding angles (127.9(3)°, 127.9(3)°) of **1′** and **2′**.[19,20] The Ni–O(methanol) (2.236(8) and 2.253(8) Å) and Ni–N (tertiary amine) (2.187(8) and 2.198(9) Å) bond lengths are similar to those of analogous complexes **1′** and **2′**.[19,20] Two planes [O(1), O(2), N(3), N(9)] and [O(1), O(3), N(7), N(10)] make an angle of 8.7°, which is slightly smaller than those (10.9°, 11.2°) of **1′** and **2′**.[19,20] The Ni···Ni distance of 3.559(2) Å is close to those (3.521(2) and 3.507(2) Å) of two analogous complexes **1′** and **2′**.[19,20] Also, the Ni···Ni distances in **1′**, **2′**, and **3′** are extremely close to that (3.5 Å) in urease of KAU.[3]

Synthesis and Structures of the Dinuclear Nickel(II) Complexes Containing Urea as an Urease Model. The dinuclear nickel(II) complexes **6**–**10** containing urea were synthesized by the reaction between **1**, **2**, **3**, **4** or **5** and **2** equivalent of urea in acetone at room temperature. However, these urea complexes **6**–**10** were not obtained when the same reaction were run in methanol solutions. For these results, we suppose that the exchange reaction between the methanol bonded to nickel(II) and methanol as solvent occurs mainly in the latter solutions. The IR spectra of **6**–**10** show the carbonyl stretching frequency of urea coordinated through its oxygen atom.[13] Furthermore, these complexes show the sharp bands in the range of 1572 to 1683 cm^{-1} (ν_{as} (COO)) (Table 2). The electronic absorption spectra of **6**–**10** in solid state are typical of a six-coordinate octahedral geometry about each nickel(II) with bands in the three regions: 980–1020, 620–660, and 380–390 nm (Table 2).[13,19,20] From these results and elemental analysis, the complexes **6**–**10** containing urea are considered to have the

Table 3. Selected Bond Lengths and Bond Angles for Compound **3′**

Bond lengths (Å)			
Ni(1)···Ni(2)	3.559(2)	Ni(1)–O(1)	1.959(6)
Ni(1)–O(2)	2.025(8)	Ni(1)–O(4)	2.236(8)
Ni(1)–N(1)	2.050(8)	Ni(1)–N(3)	2.027(9)
Ni(1)–N(9)	2.187(8)	Ni(2)–O(1)	1.982(7)
Ni(2)–O(3)	2.043(7)	Ni(2)–O(5)	2.253(8)
Ni(2)–N(5)	2.049(9)	Ni(2)–N(7)	2.065(8)
Ni(2)–N(10)	2.198(9)	O(1)–C(1)	1.40(1)
O(2)–C(4)	1.20(1)	O(3)–C(4)	1.28(1)
O(4)–C(6)	1.41(2)	O(5)–C(7)	1.41(2)
Bond angles (°)			
O(1)–Ni(1)–O(2)	96.7(3)	O(1)–Ni(1)–N(1)	93.0(3)
O(2)–Ni(1)–N(3)	99.6(3)	N(1)–Ni(1)–N(3)	96.3(3)
O(1)–Ni(1)–N(9)	83.3(3)	O(2)–Ni(1)–N(9)	178.0(3)
O(1)–Ni(1)–O(4)	81.3(3)	O(2)–Ni(1)–O(4)	86.7(3)
O(1)–Ni(2)–O(3)	96.4(3)	O(1)–Ni(2)–N(10)	80.6(3)
O(3)–Ni(2)–N(7)	102.9(3)	N(7)–Ni(2)–N(10)	80.0(3)
O(1)–Ni(2)–O(5)	82.8(3)	O(3)–Ni(2)–O(5)	85.1(3)
O(1)–Ni(2)–N(5)	99.6(3)	O(3)–Ni(2)–N(5)	98.1(3)
Ni(1)–O(1)–Ni(2)	129.0(3)	Ni(1)–O(2)–C(4)	132.7(7)
Ni(2)–O(3)–C(4)	131.2(7)		



1	$R = CH_3$,	$X = Y = H_2O$	
1'	$R = CH_3$,	$X = Y = CH_3OH$	
2	$R = C_2H_5$,	$X = Y = H_2O$	
2'	$R = C_2H_5$,	$X = Y = CH_3OH$	
3	$R = CH_2Cl$,	$X = Y = H_2O$	
3'	$R = CH_2Cl$,	$X = Y = CH_3OH$	
4	$R = CCl_3$,	$X = Y = H_2O$	
5	$R = CF_3$,	$X = Y = H_2O$	
6 (6')	$R = CH_3$,	$X = H_2O$,	Y = urea
7	$R = C_2H_5$,	$X = H_2O$,	Y = urea
8	$R = CH_2Cl$,	$X = H_2O$,	Y = urea
9	$R = CCl_3$,	$X = H_2O$,	Y = urea
10	$R = CF_3$,	$X = H_2O$,	Y = urea

Chart 1. Structure I.

dimeric structure I (Chart 1), in which one coordinated water molecule in **1**–**5** is displaced by an urea.

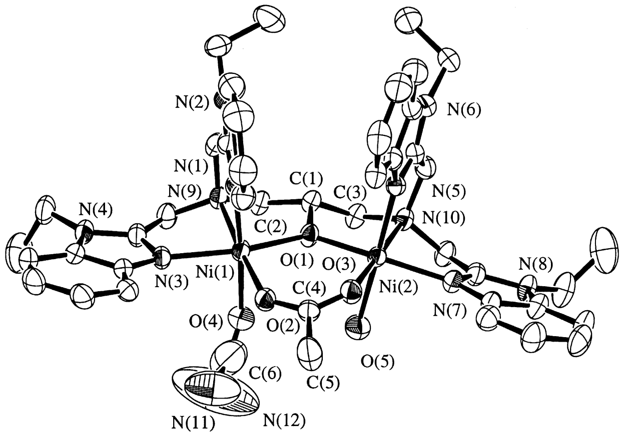


Fig. 2. An ORTEP drawing of $[Ni_2(L\text{-}Et(OAc)(ur)(H_2O)]^{2+}$ of **6′** with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

Table 4. Selected Bond Lengths and Bond Angles for Compound **6′**

Bond lengths (Å)			
Ni(1)···Ni(2)	3.5220(9)	Ni(1)–O(1)	1.962(3)
Ni(1)–O(2)	2.039(4)	Ni(1)–O(4)	2.227(6)
Ni(1)–N(1)	2.036(5)	Ni(1)–N(3)	2.062(4)
Ni(1)–N(9)	2.177(4)	Ni(2)–O(1)	1.950(3)
Ni(2)–O(3)	2.045(4)	Ni(2)–O(5)	2.162(4)
Ni(2)–N(5)	2.060(2)	Ni(2)–N(7)	2.056(4)
Ni(2)–N(10)	2.191(5)	O(1)–C(1)	1.395(6)
O(2)–C(4)	1.261(6)	O(3)–C(4)	1.238(7)
O(4)–C(6)	1.10(2)	N(11)–C(6)	1.51(2)
N(12)–C(6)	1.59(2)		
Bond angles (°)			
O(1)–Ni(1)–O(2)	96.7(1)	O(1)–Ni(1)–N(1)	96.3(2)
O(2)–Ni(1)–N(3)	102.1(6)	N(1)–Ni(1)–N(3)	88.3(2)
N(3)–Ni(1)–N(9)	80.3(2)	O(1)–Ni(1)–N(9)	80.8(1)
O(2)–Ni(1)–N(9)	177.6(2)	O(1)–Ni(1)–O(4)	85.1(2)
O(2)–Ni(1)–O(4)	87.4(2)	O(1)–Ni(2)–O(3)	97.0(1)
O(1)–Ni(2)–N(10)	82.9(1)	O(3)–Ni(2)–N(7)	101.2(2)
N(7)–Ni(2)–N(10)	78.9(2)	O(1)–Ni(2)–O(5)	82.4(2)
O(3)–Ni(2)–O(5)	88.0(2)	O(1)–Ni(2)–N(5)	94.9(2)
O(3)–Ni(2)–N(5)	98.7(2)	O(4)–C(6)–N(11)	116(1)
O(4)–C(6)–N(12)	133(1)	O(2)–C(4)–C(5)	116.3(5)
O(3)–C(4)–C(5)	116.8(5)	Ni(1)–O(1)–Ni(2)	128.4(2)
Ni(1)–O(2)–C(4)	134.1(4)	Ni(2)–O(3)–C(4)	132.4(4)

The Crystal and Molecular Structure of $[Ni_2(L\text{-}Et)(OAc)(ur)(H_2O)](ClO_4)_2\cdot 2(CH_3)_2CO$, 6′. The structure of the complex cation and the atom labelling scheme are shown in Fig. 2. Selected bond lengths and angles are given in Table 4. Each nickel(II) center has an octahedral geometry with an N_3O_3 donor set from a bridging acetato, an alkoxo of L-Et^-, an urea molecule or a water molecule, a tertiary amino nitrogen and two imidazolyl nitrogen of L-Et^-. That is, a monodentate urea molecule coordinates through its oxygen atom O(4) to Ni(1), while the methanol ligand bound for Ni(2) of **1′** have now been replaced by water molecule. As we can see from Ta-

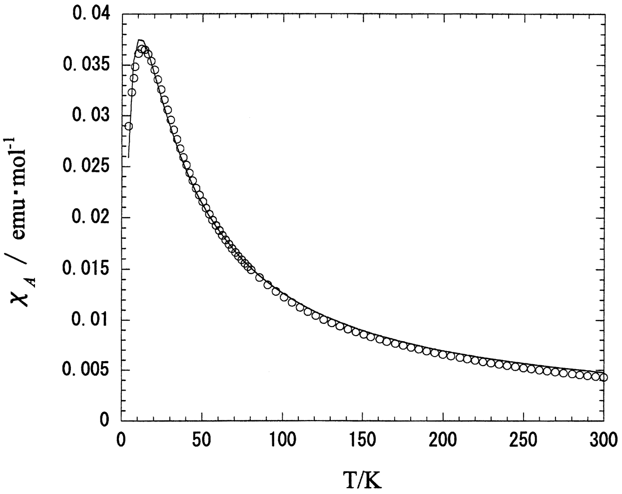


Fig. 3. Temperature dependence of the magnetic susceptibility of **6**. The open circles indicate observed susceptibility. The solid line shows the theoretical susceptibility calculated by Eq. 1.[26]

ble 4, **6′** and **1′** are isostructural, with quite similar overall geometries and dimensions involving the ligands and the nickel centers. The Ni···Ni separation is 3.5220(9) Å, which is quite close to those (3.521(2), 3.507(2), and 3.5 Å for **1′**, **2′** and urease of KAU, respectively) of three analogous complexes **1′**,[20] **2′**,[20] **3′** and the bacterial urease of KAU.[2] The similar Ni···Ni separation (3.4749(6) Å) is seen in the complex [Ni_2(OAc)$_3$(ur)(tmen)$_2$](OTf) (tmen = *N,N,N′,N′*-tetramethylethylenediamine, OTf = trifrate anion).[12] The Ni-O(ur) distance of 2.227(6) Å is rather longer than those (2.070(2), 2.063(4) Å) of analogous dinickel(II) urea complexes.[12,17] The dihedral angle between [O(1), O(2), N(3), N(9)] and [O(1), O(3), N(7), N(10)] is 12.1°, which is similar to those (10.9° and 11.2°) of **1′** and **2′**.[20]

Magnetic Properties of the Complexes 3–10. The magnetic moments at room temperature are given in Table 2. The magnetic moments of complexes **3–5** and urea containing complexes **6–10** are close to those of high-spin mononuclear nickel(II) or dinuclear nickel(II) complexes without nickel(II)–nickel(II) interaction. In order to obtain detailed information on the magnetic properties of these complexes, the magnetic susceptibilities of **5**, **6**, **8**, and **10** were measured over the temperature range from liquid helium temperature to room temperature. A typical example of the data is shown in Fig. 3. The magnetic susceptibility of **6** shows a peak near 10 K and a decrease at lower temperature (Fig. 3), indicating an antiferromagnetic interaction within the dinuclear complex of **6**. The magnetic parameters, g, $2J$, and p can be estimated from the best fit of the χ_A value to Eq. 1[26] based on the isotropic Heisenberg model ($H = -2J\,S_1 \cdot S_2$, $S_1 = S_2 = 1$):

$$\chi_A = \frac{Ng^2\beta^2}{kT} \times \frac{[5+\exp(4x)](1-p)}{5+3\exp(4x)+\exp(6x)} + \frac{(2Ng^2\beta^2)p}{3kT} \tag{1}$$

where x, g and p are $-J/kT$ (J is the exchange integral), the g factor and the rate of the paramagnetic impurity, respectively. To take into account the intercluster exchange interactions for the complexes **5**, **6**, **8**, and **10**, a molecular field correction term is added to Eq. 1. The equation for exchange-corrected susceptibility then has the form:

$$\chi_A' = \frac{\chi_A}{1-(2zJ'/Ng^2\beta^2)\chi_A} \tag{2}$$

where χ_A is the susceptibility calculated from Eq. 1, J' is the intercluster-exchange constant and z is the number of interacting nearest neighbours. The best fit to Eq. 2 to the data were found with $g = 2.47$, $2J = -15.8$ cm^{-1}, $2J' = -6.8$ cm^{-1}, and $p = 0$ for **6**. The magnetic parameters for the complexes **5**, **8**, and **10** were also obtained by the same method, and those are listed in Table 5. These $2J$ values indicate antiferromagnetic exchange interaction between the nickel(II) centers for **5**, **6**, **8**, and **10**. These facts are very similar to those of **1** and **2**. However, in spite of the resemblance of the structures for **1′** and its urea complex **6′**, considerable difference in $2J$ values of **1** and **6** corresponding to **1′** and **6′** is observed (Table 5). We suppose that a slight structural change affects the magnetic interaction. The magnetic properties of some dinuclear nickel(II) complexes with an urea have been reported.[12,16,17] [Ni_2(μ-OAc)$_3$(ur)(tmen)$_2$](OTf) ($2J = -1.8$ cm^{-1})[12] and [Ni_2(μ-OAc)(ur)(L)](ClO$_4$)$_2$ ($2J = -2.6$ cm^{-1}, L = 3,5-bis{*N,N*-bis[2-(ethylsulfanyl)ethyl]aminoethyl}pyrazolato)[17] are weakly antiferromagnetically exchange-coupled. On the other hand, a ferromagnetic exchange interaction was reported for [Ni_2(L′)(NCS)$_3$(ur)] ($2J = +20.0$ cm^{-1}), where L′ is 2-{*N*-[2-(dimethylamino)ethyl] iminomethyl}-6-{*N*-methyl *N*-[2-(dimethylamino)ethyl]aminomethyl}-4-bromophenol.[16] The magnetic properties of the present urea complexes **6**, **8**, and **10** are similar to that ($2J = -12.6$ cm^{-1}) of jack bean urease,[27] which is free from an urea as substrate.

In conclusion, the coordination of the complexes **6–10** containing an urea molecule is unsymmetric and each nickel(II) ion is in a distorted octahedral environment. On the other hand, the coordination geometry around the two nickel(II) in two kinds of bacterial urease is non-equivalent, as mentioned above.[2,5] However, the structures of **6–10** are similar to the active sites of the native urease in several points: (i) one carboxylate ligand bridges two nickel(i) ions in Ni–O–C–O–Ni fashion, which is seen in bacterial urease; (ii) Each nickel(II) is coordinated by two imidazolato groups; (iii) The Ni···Ni distance in the dinuclear complex **6′** is extremely close to that (3.5 Å) in the urease of KAU; (iv) The antiferromagnetic interactions between the two nickel(II) ions in the urea containing complexes **6**, **8**, and **10** are also seen in the magnetic datum ($2J = -12.6$

Table 5. The Magnetic Parameters of Complexes **1**, **2**, **5**, **6**, **8** and **10**

Complex	g	$2J$ / cm^{-1}	$2J'$ / cm^{-1}	z	P / %	Ref.
1	2.24	−43.2			0.044	20
2	2.09	−34.4			0	20
5	2.21	−13.8	−3.8	4	0	This work
6	2.47	−15.8	−6.8	4	0	This work
8	2.28	−8.0	−6.1	4	0	This work
10	2.03	−13.3		0	0	This work

cm^{-1}) for jack bean urease.[27]

At last, in connection with the research for function models of urease, a conversion of urea into ethyl carbamate was preliminarily examined in ethanol-acetonitorile (1 : 1 by volume) for complex **6**. The reaction was carried out at 80 °C for 2 d, however, no formation of ethyl carbamate can be observed. Its reason is quite unknown at the present stage.

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