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# Synthesis and structures of urea-coordinated dinickel(II) complexes with binucleating ligand 1,3-bis(N-(2-(dimethylamino)ethyl)-N-methylamino) propan-2-ol (**HL**<sup>1</sup>) and its analogs



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#### ABSTRACT

New urea-coordinated dinickel(II) complexes with binucleating ligands–**HL**<sup>1</sup>, which contains dimethylaminoethyl arms, and its analogs **HL**<sup>2</sup>, which features bis(methoxyethyl) arms, and **HL**<sup>3</sup>, which contains one dimethylaminoethyl arm and one bis(methoxyethyl) arm–all of which contain a 2-hydroxytrimethylene bridge between the two chelating sites, were synthesized. The structures of  $[Ni_2L^1(\mu-CH_3COO)$ (CH<sub>3</sub>COO)(urea)(EtOH)]BPh<sub>4</sub>-EtOH (**2**),  $[Ni_2L^1(\mu-Cl)_2(urea)(CH_3CN)]BPh_4·H_2O$  (**3**),  $[Ni_2L^2(H_2O)_2(urea)$ Cl](BPh<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**5**), and  $[Ni_2L^3(\mu-CH_3COO)_2(urea)]BPh_4$  (**7**) were revealed by X-ray crystallography, as well as those of their parent dinickel(II) complexes,  $[Ni_2L^1(\mu-CH_3COO)(CH_3COO)(H_2O)_2]BPh_4$  (**1**),  $[Ni_2L^2$ ( $\mu$ -CH<sub>3</sub>COO)<sub>2</sub>]BPh<sub>4</sub>·CH<sub>3</sub>CN (**4**), and  $[Ni_2L^3(\mu-CH_3COO)(CH_3COO)(EtOH)]BPh_4$  (**6**). One urea molecule was coordinated to one dinuclear nickel(II) ion, forming intramolecular hydrogen bonds with a  $\mu$ -acetato bridge (**2**, **7**), a  $\mu$ -chloro bridge (**3**), and coordinated chloro and aqua ligands (**5**). The formation of **7** from the reaction of **6** with urea was associated with a change in coordination mode from a non-bridging acetato ligand to a  $\mu$ -acetato ligand. Magnetic measurements revealed a weak antiferromagnetic interaction between the two nickel(II) ions in **1** (J = -16.7 cm<sup>-1</sup>) and **2** (J = -15.0 cm<sup>-1</sup>).

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#### 1. Introduction

Since the active site of urease (from *Klebsiella aerogenes* [1] and *Bacillus pasteurii* [2]), a metallo-enzyme that hydrolyzes urea to ammonia and carbon dioxide, was revealed by X-ray structural analysis, a number of dinickel(II) complexes have been synthesized as active site models [3,4]. In order to design active site models bearing two nickel(II) ions, binucleating ligands, which have two chelating side arms linked by various functional groups to attract two nickel(II) ions, have been widely used [3,4]. In this way, urea-coordinated complexes have been synthesized from carboxy-lato- [5], phenolato- [6–12], alkoxo- [13,14], pyrazolato- [15–20], and phthalazine- [21] bridged dinickel(II) complexes. These urea-coordinated complexes are important in examining mechanisms for catalytic hydrolysis of urea, because they are thought to be the first intermediate in the hydrolysis reaction [3,4].

We recently reported the synthesis of binucleating ligands **HL**<sup>1</sup>, **HL**<sup>2</sup>, and **HL**<sup>3</sup>, in which two chelating sites are linked by a 2hydroxytrimethylene bridge (Scheme 1), and their use in the preparation of dizinc(II) complexes [22]. Because fewer examples of urea-coordinated complexes have been reported for binucleating ligands with an alkoxo-bridge than for those described above, we decided in the present study to synthesize urea-coordinated dinickel(II) complexes using these ligands. Their structures were revealed by X-ray structure analysis, and the magnetic behavior of dinickel(II) complexes with  $L^1$  was also investigated. In this way we elucidated the coordination behavior of urea with the dinickel(II) sites formed by our synthesized alkoxo-bridged binucleating ligands (Scheme 2).

#### 2. Experimental

#### 2.1. Synthesis of binucleating ligands

1,3-Bis(*N*-(2-(dimethylamino)ethyl)-*N*-methylamino)propan-2ol (**HL**<sup>1</sup>), 1,3-bis(bis(2-methoxyethyl)amino)propan-2-ol (**HL**<sup>2</sup>), and 1-(*N*-(2-(dimethylamino)ethyl)-*N*-methylamino)-3-(bis(2-methoxyethyl)amino)propan-2-ol (**HL**<sup>3</sup>), were synthesized by a previously reported method [22].

#### 2.2. Synthesis of nickel complexes

#### 2.2.1. $[Ni_2L^1(\mu-CH_3COO)(CH_3COO)(H_2O)_2]BPh_4$ (1)

To an ethanol solution (5 ml) of  $HL^1$  (0.10 g, 0.38 mmol) was added Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.19 g, 0.76 mmol), and the solution was heated at 60 °C for 2 h. The addition of NaBPh<sub>4</sub> (0.13 g,



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Scheme 1. Structural formulae of ligands.

0.38 mmol) resulted in a green precipitate, which was filtered and dried under vacuum (yield 0.16 g). Slow diffusion of ethyl acetate vapor into a nitromethane solution of the precipitate (nitromethane/ethyl acetate vapor diffusion method) yielded green rectangular crystals. Elemental analysis of a sample of **1** which was dried under vacuum over  $P_2O_5$  at 90 °C for 12 h gave the corresponding complex formed by the loss of one water molecule from the parent complex. *Anal.* Calc. for (C<sub>41</sub>H<sub>61</sub>N<sub>4</sub>O<sub>7</sub>B<sub>1</sub>Ni<sub>2</sub>-H<sub>2</sub>O): C, 59.18; H, 7.15; N, 6.73; C/N = 8.79. Found: C, 59.52; H, 7.23; N, 6.82%; C/N = 8.73.

#### 2.2.2. $[Ni_2L^1(\mu-CH_3COO)(CH_3COO)(urea)(EtOH)]BPh_4$ ·EtOH (2)

To an ethanol solution (5 ml) of **HL**<sup>1</sup> (0.10 g, 0.38 mmol) were added Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.19 g, 0.76 mmol) and urea (0.23 g, 3.83 mmol). After the mixture was stirred at room temperature for 2 h, addition of NaBPh<sub>4</sub> (0.13 g, 0.38 mmol) resulted in the formation of a green precipitate (0.20 g, yield: 54%), which was recrystallized from nitromethane/ethanol by the vapor diffusion method to yield green crystals. *Anal.* Calc. for C<sub>46</sub>H<sub>73</sub>N<sub>6</sub>O<sub>8</sub>B<sub>1</sub>Ni<sub>2</sub>: C, 57.18; H, 7.61; N, 8.70. Found: C, 56.83; H, 7.38; N, 8.83%. IR (KBr): v(urea) = 1668 cm<sup>-1</sup>.

#### 2.2.3. $[Ni_2L^1(\mu-Cl)_2(urea)(CH_3CN)]BPh_4 H_2O(3)$

Complex **3** was prepared by a similar method to **2**, but using nickel(II) chloride hexahydrate instead of Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O. The resulting green precipitates were recrystallized from acetonitrile/ ethyl acetate by the vapor diffusion method to afford green crystals (yield: 50%). *Anal.* Calc. for C<sub>40</sub>H<sub>58</sub>N<sub>7</sub>O<sub>2</sub>B<sub>1</sub>Cl<sub>2</sub>Ni<sub>2</sub>: C, 55.35; H, 6.73; N, 11.30. Found: C, 55.65; H, 6.75; N, 11.76%. IR:  $\nu$ (urea) = 1661 cm<sup>-1</sup>. Elemental analysis of a sample dried under vacuum over P<sub>2</sub>O<sub>5</sub> at 90 °C for 12 h, showed data corresponding to a complex formed by the loss of one acetonitrile molecule from the parent complex. *Anal.* Calc. for (C<sub>40</sub>H<sub>58</sub>N<sub>7</sub>O<sub>2</sub>B<sub>1</sub>Cl<sub>2</sub>Ni<sub>2</sub>-CH<sub>3</sub>CN): C, 55.19; H, 6.70; N, 10.16. Found: C, 55.62; H, 6.70; N, 9.91%.

#### 2.2.4. [Ni<sub>2</sub>L<sup>2</sup>(μ-CH<sub>3</sub>COO)<sub>2</sub>]BPh<sub>4</sub>·CH<sub>3</sub>CN (**4**)

Complex **4** was synthesized by the reaction of  $HL^2$  with two equivalents of Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O in ethanol using a similar method to that used for the preparation of complex **1**. However, the reaction carried out in the presence of excess urea did not give urea-coordinated complexes. The crude product was recrystallized from acetonitrile/ethyl acetate by the vapor diffusion method to give green crystals (yield: 50%). A sample dried under vacuum at 80 °C was used for elemental analysis. *Anal.* Calc. for C<sub>43</sub>H<sub>59</sub>N<sub>2</sub>O<sub>9</sub>B<sub>1</sub>Ni<sub>2</sub>: C, 59.79; H, 7.93; N, 8.37. Found: C, 58.92; H, 6.80; N, 8.24%.

#### 2.2.5. $[Ni_2 L^2(H_2 O)_2(urea)Cl](BPh_4)_2 \cdot H_2 O$ (**5**)

Complex **5** was prepared by the procedure described for **3**, but using **HL**<sup>2</sup> instead of **HL**<sup>1</sup>. The crude product was recrystallized from nitromethane/ethanol by the vapor diffusion method to give green crystals (yield: 68%). *Anal.* Calc. for C<sub>64</sub>H<sub>83</sub>N<sub>4</sub>O<sub>9</sub>B<sub>1</sub>Cl<sub>1</sub>Ni<sub>2</sub>: C, 62.66; H, 6.82; N, 4.57. Found: C, 62.62; H, 6.73; N, 4.69%. IR (KBr): v(urea) = 1640 cm<sup>-1</sup>.

#### 2.2.6. [Ni<sub>2</sub>L<sup>3</sup>(µ-CH<sub>3</sub>COO)(CH<sub>3</sub>COO)(EtOH)]BPh<sub>4</sub> (**6**)

To a methanol solution (4 ml) of **HL**<sup>3</sup> (0.10 g, 0.34 mmol) was added Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.17 g, 0.68 mmol), and the mixture was heated at 60 °C for 2 h. Addition of NaBPh<sub>4</sub> (0.12 g, 0.85 mol) gave a green precipitate, which was filtered, washed with methanol, and dried under vacuum. The product was recrystallized from nitromethane/ethanol by vapor diffusion to afford green crystals (yield: 56%). *Anal.* Calc. for C<sub>44</sub>H<sub>64</sub>N<sub>3</sub>O<sub>8</sub>B<sub>1</sub>Ni<sub>2</sub>: C, 59.30; H, 7.24; N, 4.72. Found: C, 59.25; H, 7.28; N, 4.79%. IR (KBr):  $v(\mu$ -CH<sub>3</sub>-COO) = 1595 cm<sup>-1</sup>,  $v(CH_3COO) = 1551$  cm<sup>-1</sup>.

#### 2.2.7. $[Ni_2 L^3(\mu-CH_3COO)_2(urea)]BPh_4$ (7)

To a nitromethane solution (2 ml) of complex **6** (0.25 g, 0.28 mmol) was added an excess amount of urea (0.10 g, 1.67 mmol) in a solution of ethanol (0.2 ml). The mixture was heated at 60 °C for 2 h. After the mixture was cooled to room temperature, the precipitated urea was filtered off. Slow diffusion of ethyl acetate into the filtrate yielded green crystals (yield: 48%). *Anal.* Calc. for  $C_{43}H_{62}N_5O_8B_1Ni_2$ : C, 57.06; H, 6.90; N, 7.74. Found: C, 57.04; H, 6.62; N, 7.72%. IR (KBr):  $v(\text{urea}) = 1672 \text{ cm}^{-1}$ ,  $v(\mu - \text{CH}_3\text{COO}) = 1600 \text{ cm}^{-1}$ .

#### 2.3. Physical measurements

Elemental analyses were performed by the Center for Instrumental Analysis at Hokkaido University. Magnetic susceptibilities were measured using a Quantum MPMS-XL SQUID magnetometer. Visible absorption spectra were measured using a Varian Cary 500 spectrophotometer and a JASCO V-650 spectrophotometer with an integrating sphere. IR spectra were measured using a Shimadzu FT-IR-8300 spectrophotometer.

#### 2.4. Crystallographic studies

X-ray crystallography of single crystals was carried out using a Mac Science MXC3 k four-circle diffractometer (**2**, **3**, and **5**) and a Rigaku XtaLAB-mini (**1**, **4**, **6**, and **7**) diffractometer with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  or 0.71075 Å). The structures were solved by the direct method (SIR92, SIR97,



Scheme 2. Structural formulae of complexes.

SIR2004, SIR2008 [23]), and refined on  $F^2$  by the full-matrix leastsquares method using SHELXL 97 [24]). A  $\varphi$ -scan was applied for absorption correction [25] of **2**, **3**, and **5**, as well as numerical absorption correction of **1**, **4**, **6**, and **7**. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were placed by SHELXL [24] (riding model refinement). Calculations were carried out using the MAXUS program system provided by Mac Science (using a SiliconGraphics O<sub>2</sub> work station) and the CRYSTALSTRUCTURE program (ver. 4.0) provided by Rigaku (using a personal computer with WINDOWS XP os). Structural diagrams were drawn using ORTEP-3 for Windows [26]. Crystallographic data for the complexes are listed in Table 1.

#### 3. Results and discussion

The reaction of the binucleating ligand **HL**<sup>1</sup> with Ni(CH<sub>3</sub>COO)<sub>2</sub>· 4H<sub>2</sub>O in ethanol at a molar ratio of **HL**<sup>1</sup>:Ni = 1:2 resulted in the formation of the dinuclear nickel(II) complex [Ni<sub>2</sub>L<sup>1</sup>( $\mu$ -CH<sub>3</sub>COO)(CH<sub>3</sub>-COO)(H<sub>2</sub>O)<sub>2</sub>]BPh<sub>4</sub> (1), in which the deprotonated species L<sup>1</sup> acted as a *N*,*N*,*N*,*N*-pentadentate ligand and the two nickel(II) ions were linked by a  $\mu$ -alkoxo bridge and a  $\mu$ -acetato bridge; the Ni···Ni distance was 3.5479(7) Å and the Ni(1)–O(20)–Ni(2) angle was 123.89(10)° (Fig. 1 and Table 2). Although **HL**<sup>1</sup> is a binucleating ligand with symmetrical chelating side arms with respect to the central 2-hydroxytrimethylene bridge, the two six-coordinated

Table 1			
Crystallographic	data	of	complexes.

Complex	1	2	3	4	5	6	7
Empirical formula	$B_1 C_{41} H_{61} N_4 N i_2 O_7 \\$	$B_1 C_{46} H_{73} N_6 Ni_2 O_8 \\$	$B_1 C_{40} H_{60} C l_2 N_7 N i_2 O_3 \\$	$B_1 C_{45} H_{62} N_3 Ni_2 O_9$	$B_2 C_{64} H_{83} Cl_1 N_4 Ni_2 O_9$	$B_1 C_{44} H_{64} N_3 Ni_2 O_8$	$B_1 C_{43} H_{62} N_5 Ni_2 O_8 \\$
Formula weight	850.13	966.33	886.08	917.21	1226.83	891.21	905.20
T (K)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
$\lambda$ (Å)	0.71075	0.71073	0.71075	0.71075	0.71073	0.71075	0.71075
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	ΡĪ	ΡĪ	$P2_1/c$	$P2_1/c$
a (Å)	15.7424(17)	17.591(8)	18.230(3)	11.618(7)	11.765(3)	14.169(6)	11.254(5)
b (Å)	12.1464(11)	17.449(5)	15.284(3)	14.000(8)	14.4120(14)	18.064(7)	15.027(6)
c (Å)	23.968(4)	17.256(7)	16.364(4)	14.870(8)	18.5460(18)	18.342(8)	27.273(10)
α (°)				76.444(15)	95.475(8)		
β (°)	107.058(5)	104.69(4)	101.445(16)	84.969(18)	91.001(12)	98.824(4)	91.374(5)
γ (°)				86.123(17)	93.904(12)		
$V(Å^3)$	4381.4(9)	5124(4)	4468.8(15)	2339(3)	3122.1(8)	4639(4)	4611(3)
Ζ	4	4	4	2	2	4	4
$D_{\rm calc}~({ m Mg}~{ m m}^{-3})$	1.286	1.253	1.317	1.302	1.305	1.276	1.304
$\mu$ (mm $^{-1}$ )	0.910	0.788	1.006	0.860	0.704	0.863	0.871
F(000)	1800	2064	1872	972	1300	1896	1920
Crystal size (mm)	$0.50 \times 0.20 \times 0.12$	$\textbf{0.90} \times \textbf{0.80} \times \textbf{0.60}$	$0.50 \times 0.40 \times 0.15$	$\textbf{0.61} \times \textbf{0.46} \times \textbf{0.16}$	$0.70 \times 0.50 \times 0.35$	$\textbf{0.62} \times \textbf{0.48} \times \textbf{0.11}$	$0.79 \times 0.50 \times 0.50$
Number of reflections	8950	11712	10247	10603	14341	10648	10581
Goodness-of-fit (GOF) on F <sup>2</sup>	1.064	1.015	1.024	1.059	1.024	1.099	1.063
Final R indices	$R_1 = 0.0583$ ,	$R_1 = 0.0586$ ,	$R_1 = 0.0763$ ,	$R_1 = 0.0531$ ,	$R_1 = 0.0387$ ,	$R_1 = 0.0476$ ,	$R_1 = 0.0599,$
$[I > 2\sigma(I)]$	$wR_2 = 0.1595$	$wR_2 = 0.1586$	$wR_2 = 0.2124$	$wR_2 = 0.1502$	$wR_2 = 0.1049$	$wR_2 = 0.1197$	$wR_2 = 0.1615$
Largest difference in	0.830 and -0.450	0.560 and -0.533	1.403 and -0.4123	0.840 and -0.910	0.617 and -0.417	0.32 and -0.44	0.810 and -0.620
peak and hole (e Å <sup>-3</sup> )							



**Fig. 1.** ORTEP Drawing of the cation section of **1**,  $[Ni_2L^1(\mu-CH_3COO)(CH_3COO)(H_2-O)_2]^*$ , with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–O(20) 1.997(2), Ni(1)–O(32) 2.038(3), Ni(1)–O(42) 2.166(3), Ni(1)–O(43) 2.202(3), Ni(1)–N(1) 2.128(3), Ni(1)–N(4) 2.143(4), Ni(2)–O(20) 2.024(3), Ni(2)–O(33) 2.030(3), Ni(2)–O(51) 2.130(4), Ni(2)–O(52) 2.144(4), Ni(2)–N(8) 2.089(3), Ni(2)–N(11) 2.136(4); O(20)–Ni(1)–O(32) 95.92(10), O(42)–Ni(1)–O(43) 59.90(9), N(1)–Ni(1)–N(4) 83.48(12), O(20)–Ni(2)–O(33) 94.94(10), O(51)–Ni(2)–O(52) 84.90(12), N(8)–Ni(2)–N(11) 84.55(13), Ni(1)–O(20)–Ni(2) 123.89(10).

nickel(II) ions had different co-ordination environments; one nickel(II) ion was associated with one bidentate acetato ligand and the other nickel(II) ion with two water molecules. The two side arms containing N(1) and N(11), respectively, adopted a *syn*-geometry with respect to the plane comprised N(4), O(20), and N(8). Complex **1** had an intramolecular hydrogen bond around the binuclear site  $(O(52)\cdots O(43) 2.763(4) Å)$ , and also intermolecular hydrogen bonds  $(O(52)\cdots O(32)\# (-x+1, y+1/2, -z+3/2) 2.853(4) Å$  and  $O(51)\cdots O(42)\# (-x+1, y+1/2, -z+3/2) 2.714(4) Å)$ . These intermolecular hydrogen bonds further connected the cation parts of **1** to form a linear chain, which was similar to that found in **2** (see below).

In contrast, the formation of a complex between  $HL^1$  and Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O in the presence of excess urea, under reaction conditions which were the same as those described for 1, followed by recrystallization from nitromethane/ethanol, gave the ureacoordinated nickel(II) complex  $[Ni_2L^1(\mu-CH_3COO)(CH_3COO)(urea)]$ (EtOH)]BPh<sub>4</sub>·EtOH (2) (Fig. 2a). The coordination mode of the binucleating ligand L<sup>1</sup> in 2 was similar to that found in 1. L<sup>1</sup> was coordinated as a pentadentate ligand, while the two six-coordinate nickel(II) ions were also linked by a  $\mu$ -alkoxo and a  $\mu$ -acetato bridges; the Ni…Ni distance was 3.545(1)Å and the Ni(1)-O(20)–Ni(2) angle was 124.53(11)°. One urea molecule was coordinated to Ni(2) through the O(53) oxygen atom (Ni(2)–O(53): 2.062(3)Å) as a planar molecule. The bond lengths of C(50)-O(53) (1.250(4) Å), C(50)–N(51) (1.329(5) Å), and C(50)–N(52) (1.335(5) Å) were similar to those found in other urea-coordinated nickel complexes (see Table 2) [5-21]. In addition, the N(51) nitrogen atom of the coordinated urea interacted with the O(33) oxygen atom of the µ-acetato bridge through an intramolecular hydrogen bond  $(N(51) \cdots O(33)$ : 2.831(5)Å) and formed an intermolecular hydrogen bond with O(42)# (-x + 1/2 + 1, y + 1/2, -z + 1/2) $(N(51) \cdots O(42)$ #: 2.857(5)Å) of the acetato ligand coordinated to Ni(1). These hydrogen bonds successively connected the cation parts of **2** to form a zigzag linear chain, similar to **1** (see Fig. 2b). In addition, one oxygen atom (O(63)) of the lattice solvent, ethanol, was located close to N(52) of the urea molecule  $(O(63) \cdots N(52))$ : 3.073(9) Å). Another intramolecular hydrogen bond was observed between O(62) of the ethanol molecule coordinated to Ni(2) and O(43) of the acetato ligand coordinated to Ni(1) (O(62)...O(43):

Table 2	
Structural	data

() <sup>a</sup>
-

<sup>a</sup> Averaged values.



**Fig. 2.** (a) ORTEP Drawing of the cation section of **2**, [Ni<sub>2</sub>L<sup>1</sup>(μ-CH<sub>3</sub>COO)(CH<sub>3</sub>COO)(urea)(EtOH)]<sup>+</sup>, with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–O(20) 1.987(2), Ni(1)–O(32) 2.042(3), Ni(1)–N(4) 2.126(3), Ni(1)–N(1) 2.128(3), Ni(1)–O(42) 2.139(3), Ni(1)–O(43) 2.219(3), Ni(2)–O(20) 2.018(2), Ni(2)–O(33) 2.029(3), Ni(2)–O(53) 2.062(3), Ni(2)–N(8) 2.114(4), Ni(2)–O(62) 2.140(3), Ni(2)–N(11) 2.158(4), N(52)–C(50) 1.335(5), N(51)–C(50) 1.329(5), O(53)–C(50) 1.250(4); O(20)–Ni(1)–O(32) 96.28(10), O(42)–Ni(1)–O(43) 59.95(10), O(53)–Ni(2)–O(62) 85.61(11), Ni(1)–O(20)–Ni(2) 124.53(11), O(53)–C(50)–N(51) 122.8(4), O(53)–C(50)–N(52) 119.9(4), N(51)–C(50)–N(52) 117.3(4). (b) Hydrogen bond network of **2**.

2.721(4) Å). Similar hydrogen bonding between urea NH and the O atoms of the bridging acetate has been observed in other model systems [18]. Thus, it was suggested that hydrogen bonds play an important role in the stabilization of urea binding to the dinuclear nickel(II) site in the crystal. The formation of **2** essentially corresponded to the substitution of the coordinated water molecules of **1** by one urea and one ethanol. The reaction of **1** with urea in a nitromethane solution containing a small amount of ethanol (ca. 10%) followed by recrystallization from nitromethane/ethanol (vapor diffusion method) gave the urea-coordinated complex **2**.

#### Complex $1 + urea + EtOH \rightarrow complex 2 + 2H_2O$

The reaction of **HL**<sup>1</sup> with Ni(II)Cl<sub>2</sub>·6H<sub>2</sub>O instead of Ni(II)(CH<sub>3</sub>-COO)<sub>2</sub>·4H<sub>2</sub>O in the presence of excess urea, followed by recrystallization from acetonitrile/ethyl acetate, afforded the ureacoordinated dinickel(II) complex [Ni<sub>2</sub>L<sup>1</sup>( $\mu$ -Cl)<sub>2</sub>(urea)(CH<sub>3</sub>CN)]BPh<sub>4</sub>· H<sub>2</sub>O (**3**) (Fig. 3). The coordination behavior of the pentadentate ligand L<sup>1</sup> was similar to its behavior in **1** and **2**, but the two sixcoordinated nickel(II) ions were doubly linked by two chloride anions, which resulted in a considerably shortened Ni(1)···Ni(2) distance (2.969(1) Å) and a sharper Ni(1)–O(20)–Ni(2) angle (97.13(13)°) compared to the singly  $\mu$ -acetato-bridged dinickel(II) complexes **1** and **2**. One urea molecule was coordinated to Ni(2) through the O(60) oxygen atom, also forming a hydrogen bond between N(62) and Cl(40) of the  $\mu$ -chloro bridge (N(62)···Cl(40): 3.177(5) Å).

The reaction of another binucleating ligand, **HL**<sup>2</sup>, which contains two bis(methoxyethyl)amino arms, with Ni(II)(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O gave the dinuclear nickel(II) complex [Ni<sub>2</sub>L<sup>2</sup>( $\mu$ -CH<sub>3</sub>COO)<sub>2</sub>]BPh<sub>4</sub>-·CH<sub>3</sub>CN (**4**), in which L<sup>2</sup> acted as a *O*,*O*,*O*,*O*,*O*,*O*-heptadentate ligand and two 6-coordinate nickel(II) ions were linked by an alkoxo group and two  $\mu$ -acetato bridges (Fig. 4). The Ni(1)···Ni(2) distance (3.237(2) Å) was shorter than those of the singly  $\mu$ -acetato-bridged complexes **1** and **2** (av. 3.55 Å), and accordingly, the Ni(1)–O(4)–Ni(2) angle (110.07(9)°) was smaller than those of **1** and **2** (av. 124°). Because **4**–which had no coordinated solvent



**Fig. 3.** ORTEP Drawing of the cation section of **3**,  $[Ni_2L^1(\mu-Cl)_2(urea)(CH_3CN)]^+$ , with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–O(20) 1.976(3), Ni(1)–N(32) 2.071(4), Ni(1)–N(4) 2.079(4), Ni(1)–N(1) 2.115(4), Ni(1)–Cl(40) 2.4579(14), Ni(1)–Cl(50) 2.6271(16), Ni(2)–O(20) 1.983(3), Ni(2)–O(60) 2.041(3), Ni(2)–N(8) 2.102(4), Ni(2)–N(11) 2.138(4), Ni(2)–Cl(40) 2.5065(15), Ni(2)–Cl(50) 2.5542(16), O(60)–C(61) 1.242(6), N(62)–C(61) 1.332(7), N(63)–C(61) 1.330(6); Ni(1)–O(20)–Ni(2) 97.13(13), Ni(1)–Cl(40)–Ni(2) 73.44(4), Ni(2)–Cl(50)–Ni(1) 69.89(4), O(60)–C(61)–N(63) 120.3(5), O(60)–C(61)–N(62) 123.1(5), N(63)–C(61)–N(62) 116.5(5).



**Fig. 4.** ORTEP Drawing of the cation section of **4**,  $[Ni_2L^2(\mu-CH_3COO)_2]^+$ , with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–O(32) 2.035(3), Ni(1)–O(6) 2.170(3), Ni(1)–O(22) 1.974(3), Ni(1)–O(42) 2.013(3), Ni(1)–O(2) 2.138(3), Ni(1)–N(9) 2.094(4), Ni(2)–O(33) 2.059(3), Ni(2)–O(43) 1.980(3), Ni(2)–O(22) 1.975(3), Ni(2)–O(20) 2.196(4), Ni(2)–N(13) 2.051(3); Ni(1)–O(22) -Ni(2) 110.07(9).

molecules, as the coordination sites of the two nickel(II) ions were fully occupied by  $L^2$  and the bridging acetate ligands—was relatively stable, the reaction of **4** with excess urea did not afford urea-coordinated complexes. In addition, complex formation between Ni(II)(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and **HL**<sup>2</sup>, even in the presence of urea, did not afford urea-coordinated complexes but gave **4**. However, changing the counter anion from acetate to chloride resulted in a considerable alteration of the bridging mode between the two nickel(II) ions and enabled the coordination of urea to the dinickel(II) site formed by L<sup>2</sup>.

Complex formation between  $HL^2$  and  $Ni(II)Cl_2 \cdot 6H_2O$  gave the urea-coordinated dinickel(II) complex  $[Ni_2L^2(H_2O)_2(urea)Cl]$ 

(BPh<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**5**) (Fig. 5). In **5**, **L**<sup>2</sup> acted as a O,O,N,O,N,O,O-heptadentate ligand, in which only an alkoxo group linked the two nickel(II) ions, without any other bridging ligands. In this way it differed from **2** and **4**, which contained  $\mu$ -acetato bridges. The Ni(II)  $\cdots$  Ni(II) distance was 3.647(1) Å and the Ni(1)-O(4)-Ni(2) angle was 133.11(7)°; these values were the longest and the largest, respectively, among the dinickel(II) complexes synthesized in this study. One urea was also coordinated to Ni(1) through the oxygen atom O(40), forming a hydrogen bond between the nitrogen atom N(42) of the urea and Cl(30) coordinated to Ni(1) (N(42) $\cdots$ Cl(30): 3.235(3) Å). The Cl(30) atom further interacted through hydrogen bonding with O(60) of the water molecule coordinated with Ni(2) (Cl(30) $\cdots$ O(60): 3.043(2) Å). A significant feature of this complex was the positional relationship between the urea molecule coordinated with Ni(1) and the water molecule coordinated with Ni(2). The distance between O(50) of the water molecule and O(40) of the coordinated urea was quite short (2.747(2) Å), suggesting the existence of a hydrogen bonding interaction between them. Because of this, O(50) of the water molecule was located closely to the carbonyl carbon C(41) of the urea molecule  $(O(50) \cdots C(41)$ : 3.473(3)Å). We consider this positional relationship to be interesting, because it resembles a proposed intermediate for a urea hydrolysis mechanism in which one terminal hydroxide ion attacks the carbonyl carbon of urea in binuclear nickel(II) sites [3,4]. The possibility of using 5 in urea hydrolysis reactions is currently under investigation.

A non-symmetric binucleating ligand, **HL**<sup>3</sup>, which contained one *N*,*N*-dimethylaminoethyl and one bis(methoxyethyl)amino arm (a mixture of the arms of **HL**<sup>1</sup> and those of **HL**<sup>2</sup>) also afforded a binuclear nickel(II) complex and the corresponding urea-coordinated complex. This ligand was anticipated to show mixed coordination behavior, between that of **HL**<sup>1</sup> and that **HL**<sup>2</sup>. Complex formation between **HL**<sup>3</sup> and Ni(II)(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O followed by recrystallization from acetonitrile/ethanol gave a dinuclear nickel(II) complex, [Ni<sub>2</sub>-L<sup>3</sup>(µ-CH<sub>3</sub>COO)(CH<sub>3</sub>COO)(EtOH)]BPh<sub>4</sub> (**6**) (Fig. 6), which comprised two six-coordinate nickel(II) ions linked by an alkoxo group and one µ-acetato bridge, with a Ni(1)···Ni(2) distance of 3.470(1) Å and a Ni(1)-O(20)-Ni(2) angle of 122.49(8)°; these values were close to those of the singly µ-acetato-bridged complexes **1** and **2**.



**Fig. 5.** ORTEP Drawing of the cation section of **5.**  $[Ni_2L^2(\mu-CH_3COO)_2]^*$ , with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–O(4) 1.9771(13), Ni(1)–N(9) 2.0785(18), Ni(1)–O(2) 2.1303(16), Ni(1)–O(6) 2.1449(18), Ni(1)–O(40) 2.1779(16), Ni(1)–Cl(30) 2.3135(8), Ni(2)–O(4) 1.9978(13), Ni(2)–O(60) 2.0348(17), Ni(2)–N(13) 2.0436(18), Ni(2)–O(50) 2.0741(16), Ni(2)–O(20) 2.1146(15), Ni(2)–O(16) 2.1162(16), O(40)–C(41) 1.253(3), C(41)–N(42) 1.318(4), C(41)–N(43) 1.335(4); Ni(1)–O(4)–Ni(2) 133.11(7), O(40)–C(41)–N(42) 122.6(3), O(40)–C(41)–N(43) 119.8(3), N(42)–C(41)–N(43) 117.5(3).



**Fig. 6.** ORTEP Drawing of the cation section of **6**,  $[Ni_2L^3(\mu-CH_3COO)(CH_3-COO)(EtOH)]^*$ , with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–O(2) 2.122(2), Ni(1)–O(6) 2.155(3), Ni(1)–O(20) 1.9738(18), Ni(1)–O(32) 1.963(3), Ni(1)–O(52) 2.124(2), Ni(1)–N(9) 2.052(3), Ni(2)–O(20) 1.9847(18), Ni(2)–O(33) 2.060(2), Ni(2)–O(42) 2.217(2), Ni(2)–O(43) 2.1061(19), Ni(2)–N(13) 2.127(3), Ni(2)–N(17) 2.093(2); Ni(1)–O(20)–Ni(2) 122.50(9).



**Fig. 7.** ORTEP Drawing of the cation section of **7**,  $[Ni_2L^3(\mu-CH_3COO)_2(urea)]^*$ , with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–O(2) 2.167(3), Ni(1)–O(6) 2.156(3), Ni(1)–O(20) 1.977(3), Ni(1)–O(32) 1.993(3), Ni(1)–O(42) 2.083(3), Ni(1)–N(9) 2.080(3), Ni(2)–O(20) 2.009(3), Ni(2)–O(33) 2.096(3), Ni(2)–O(43) 2.054(3), Ni(2)–O(50) 2.116(3), Ni(2)–N(13) 2.122(4), Ni(2)–N(17) 2.147(4), O(50)–C(51) 1.247(5), N(52)–C(51) 1.340(6), N(53)–C(51) 1.340(6); Ni(1)–O(20)–Ni(2) 113.32(11), O(50)–C(51)–N(53) 121.2(4), N(52)–C(51)–N(53) 117.1(4).

The Ni(1) and the Ni(2) atoms were associated with an ethanol molecule and a non-bridging bidentate acetato ligand, respectively; they interacted with each other through a hydrogen bond  $(O(52)\cdots O(42) (2.739(3) \text{ Å})).$ 

The reaction of **6** with urea in a mixed nitromethane/ethanol solvent gave the urea-coordinated dinickel(II) complex  $[Ni_2L^3(\mu-CH_3COO)_2(urea)]BPh_4$  (**7**) (Fig. 7). In this reaction, surprisingly, there was no direct substitution of the coordinated ethanol molecule by a urea molecule, in contrast to the formation of the urea complexes of **1** and **2**, in which direct substitution of a water molecule by a urea molecule was observed (see above). The coordination of urea with the Ni(2) ion was associated with a coordination change (carboxylate shift) of the non-bridging acetato ligand on Ni(2) to become a  $\mu$ -acetato bridge (see the Experimental section

Table 3	3
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Absorption spectrum data.

Complex	$\lambda_{\rm max}/{\rm nm}~(\epsilon/{\rm mol}^{-1}~{\rm dm}^3~{\rm cm}^{-1})^{\rm a}$	$\lambda_{\rm max}/{\rm nm^b}$
1	387(83) 646(27) 1045(23)	392 651
2	391(95) 652(31) 1051(25)	391 648
3	405(76) 686(30) 1090(26)	395 676
4	395(34) 660(15) 997(34)	395 652
5	394(42) 700(14) 1017(25)	405 692
6	386(69) 647(22) 1021(30)	394 651
7	388(51) 646(18) 1023(27)	392 661

<sup>a</sup> Nitromethane solution, 298 K.

<sup>b</sup> Diffuse reflectance spectral data (350-800 nm) for solid samples.



**Fig. 8.** Temperature dependence of molar magnetic susceptibility  $(\bigcirc)$  and effective magnetic moment ( $\bullet$ ) per nickel(II) for **1** (a), and **2** (b). The solid lines represent the best-fit calculated curves corresponding to the theoretical equation.

for IR data) and subsequent release of the ethanol molecule from the Ni(1) ion. The resulting double linkage of the two nickel(II) ions by  $\mu$ -acetato bridges resulted in a smaller Ni(1)...Ni(2) distance (3.330(1)Å) and Ni(1)–O(20)–Ni(2) angle (113.3(1)°) compared with the parent complex 6. The urea molecule, which was coordinated to Ni(2) through the O(50) oxygen atom, formed an intramolecular hydrogen bond with the  $\mu$ -acetato bridge (N(52) · · · O(33) (2.823(5) Å)) and an intermolecular hydrogen bond with the methoxy oxygen atom  $(N(53) \cdots O(6) (1 - x, -1/2 + y, 1/2 - z))$ (3.018(5)Å)). The following short contacts were also observed around the coordinated urea:  $N(52) \cdots O(43)$  (3.319(5)Å) and  $N(53) \cdots O(42) (1 - x, -1/2 + y, 1/2 - z) (3.150(5) Å)$ . These results suggest that the urea molecule may favor coordination to the nickel(II) ion on the dimethylaminoethyl arm over coordination with the corresponding ion on the bis(methoxyethyl) arm, which results in the carboxylate shift.

Table 3 shows visible absorption spectral data for our synthesized dinickel(II) complexes. The absorption spectra measured in nitromethane essentially corresponded to those measured for the solid state samples (diffuse reflectance spectra). Each complex in nitromethane showed three absorption bands, around 400, 700, and 1000 nm, which were ascribed to the spin-allowed transitions from  ${}^{3}A_{2g}(F)$  (the ground state of the octahedral d<sup>8</sup> ion) to  ${}^{3}T_{1g}(P)$ ,  ${}^{3}T_{1g}(F)$ , and  ${}^{3}T_{2g}(F)$ , respectively [27]. The urea-coordinated nicke-l(II) complexes **2**, **3**, **5**, and **7** showed absorption bands at 388–405, 646–700, and 1017–1090 nm, which were similar to those (376, 425, 745, and 1060 nm) observed for jack-bean urease [28].

The close linking of two nickel(II) ions by a binucleating ligand leads to a significant magnetic interaction between the nickel(II) ions. The effective magnetic moment per nickel(II) of **1** in the solid state was found to be dependent on temperature in the range 5–300 K (Fig. 8a), decreasing gradually with decreasing temperature from 2.8 BM at 300 K. A similar temperature dependence was also observed for the urea-coordinated complex **2** (Fig. 8b). These behaviors indicate the existence of antiferromagnetic coupling between the two nickel(II) centers. The coupling constants  $J = -16.7 \text{ cm}^{-1}$  (g = 1.99,  $\rho = 0.011$ ,  $R = \Sigma(\chi_{exptl}(i) - \chi_{calcd}(i))^2/\Sigma(\chi_{exptl}(i))^2 = 4.32 \times 10^{-3}$ ) (**1**) and  $-15.0 \text{ cm}^{-1}$  (g = 2.08,  $\rho = 0.015$ ,  $R = 4.05 \times 10^{-3}$ ) (**2**) were estimated by fitting the experimental data to the following equations derived from the binuclear model (each symbol corresponds to a commonly used parameter):

$$\begin{split} \chi_m &= (1-\rho)\chi_{dim} + \rho\chi_{mono} + TIP \\ \chi_{dim} &= (2N_A g^2 \mu_B 2/kT)(\exp(2J/kT) + 5\exp(6J/kT))/(1+3\exp(2J/kT) + 5\exp(6J/kT)), \\ \chi_{mono} &= 2N_A g 2 \mu_B 2/3kT, \\ H &= -2JS_1S_2, \\ S_1 &= S_2 = 1. \end{split}$$

The fittings were appropriate for each dinickel(II) complex. The observation of similar *J* values for these complexes regardless of the presence or absence of a coordinated urea molecule suggests that a significant magnetic interaction takes place at the alkoxobridged dinuclear nickel(II) centers.

In our synthesized urea-coordinated complexes with binucleating ligands  $L^1$ ,  $L^2$ , and  $L^3$ , one urea was coordinated to one nickel(II) ion of the dinuclear nickel(II) site through a carbonyl oxygen atom, which was further stabilized by intramolecular and intermolecular hydrogen bonds in the crystalline form. Hydrogen bonding is thought to play a significant role in the coordination of urea, a weakly coordinating ligand, to the nickel(II) ions. The coordination of a urea molecule to the binuclear nickel(II) site depended on whether the bridging ligand was a  $\mu$ -acetato or  $\mu$ -chloro bridge. The use of ligand  $L^3$ , which had one arm from each of  $L^1$  and  $L^2$ , showed that the coordination of the urea molecule took place preferentially at the dimethylaminoethyl site rather than at the bis(methoxyethyl) site. The close linking of the two nickel(II) ions by the binucleating ligand  $L^1$  resulted in a weak antiferromagnetic interaction between the nickel(II) ions, as observed for 1 and 2.

#### Appendix A. Supplementary material

CCDC 908550–908556, contain the supplementary crystallographic data for complexes **1–7**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.01.036.

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