The Formation of Monomethyl Carbonato-bridged Dinuclear Nickel(II) Complexes by an Efficient CO_2 Uptake in Methanol Containing Urea Derivatives

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Monomethyl carbonato-bridged dinuclear nickel(II) complexes $[Ni_2(L)(OOC\text{-}O\text{-}CH_3)(CH_3OH)_2](ClO_4)_2 \cdot H_2O \cdot CH_3OH$, **1** and $[Ni_2(L)(OOC\text{-}O\text{-}CH_3)(H_2O)_2](ClO_4)_2 \cdot H_2O$, **2** were obtained in the presence of $[Ni_2(L)(OH)(H_2O)_2](ClO_4)_2$ and *N*-methylurea at room temperature in air, where HL is *N,N,N',N'*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane. The crystal structure of **1** was determined by X-ray crystallography and **2** was characterized by the magnetic susceptibility and visible absorption spectrum.

A number of metal complexes containing monomethyl carbonato and tetraazacycloalkanes (L') such as [14]aneN_4[1] have been prepared and characterized.[1-3] Monomethyl carbonato in the synthetic process of these metal complexes is produced by bubbling CO_2 through methanol solution of $[M(L')](ClO_4)_2$ ($M = Co^{2+}, Ni^{2+}, Cu^{2+}$) in the presence of triethylamine.[3] The feature in these reaction systems is that the macrocyclic ligands have been used for the starting metal complexes. We synthesized here two monomethyl carbonato-bridged dinuclear nickel(II) complexes $[Ni_2(L)(OOC\text{-}O\text{-}CH_3)(CH_3OH)_2](ClO_4)_2 \cdot H_2O \cdot CH_3OH$, **1** and $[Ni_2(L)(OOC\text{-}O\text{-}CH_3)(H_2O)_2](ClO_4)_2 \cdot H_2O$, **2** from the reaction mixture of $[Ni_2(L)(OH)(H_2O)_2](ClO_4)_2$,[4] *N*-methylurea and methanol without bubbling of CO_2. The formation of monomethyl carbonate in this system has the following characteristics; (i) the macrocyclic ligands for a nickel(II) complex are not utilized, (ii) an urea derivative is used instead of a basic reagent such as triethylamine.

$[Ni_2(L)(OH)(H_2O)_2](ClO_4)_2$ was prepared by a reaction between HL (1.09 g, 1.5 mmol), $Ni(ClO_4)_2 \cdot 6H_2O$ (1.10 g, 3.0 mmol), and NaOH (0.06 g, 1.5 mmol) in ethanol (20 cm^3), and then recrystallized from methanol.[5] A mixture of *N*-methylurea (0.04 g, 0.56 mmol) and $[Ni_2(L)(OH)(H_2O)_2](ClO_4)_2$ (0.31 g, 0.28 mmol) was dissolved in 30 cm^3 of methanol and stirred at room temperature for 1 h in air.[6] The reaction mixture was allowed to evaporate to bring about a yellowish green crystals $[Ni_2(L)(OOC\text{-}O\text{-}CH_3)(CH_3OH)_2](ClO_4)_2 \cdot H_2O \cdot CH_3OH$, **1**. A crystal suitable for X-ray study was sealed in a capillary tube.[7] The crystals are stable in a methanol solution, but readily turn to $[Ni_2(L)(OOC\text{-}O\text{-}CH_3)(H_2O)_2](ClO_4)_2 \cdot H_2O$, **2** upon filtration in air (0.18 g, 54% yield).[11]

An ORTEP[12] view of $[Ni_2(L)(OOC\text{-}O\text{-}CH_3)(CH_3OH)_2]^{2+}$ in **1** is shown in Figure 1 with selected bond lengths and angles. The cation in **1** consists of two nickel(II) ions bridged by one alkoxo group of L and one bidentate monomethyl carbonato. The Ni(1)-O(1)-Ni(2) angle is 128.3(5)° which is similar to those of the corresponding acetato-bridged complexes, $[Ni_2(L)(OAc)(CH_3OH)_2](ClO_4)_2 \cdot H_2O \cdot CH_3OH$[13] and $[Ni_2(tbpO)(OAc)(H_2O)](ClO_4)_2 \cdot H_2O \cdot Et_2O$.[14] The Ni(1)-O(1) and Ni(2)-O(1) distances of 1.954(9) and 1.965(9) Å are also similar to those of $[Ni_2(L)(OAc)(CH_3OH)_2](ClO_4)_2 \cdot H_2O \cdot CH_3OH$.[13] The Ni(1)-O(2) and Ni(2)-O(3) bond lengths between two oxygen atoms of monomethyl carbonato and nickel atoms are 2.026(10) and 2.01(1) Å, respectively. The coordination environment around each nickel atom has N_3O_3 donor set from a bridging monomethyl carbonato, an alkoxo of L, a methanol molecule, a tertiary amino and two imidazolyl nitrogen atoms of L. The planes defined by O(1), O(2), N(3), N(9), and Ni(1) atoms, and O(1), O(3), N(7), N(10), and Ni(2) atoms are almost planar; maximum deviation of the atom is 0.14 Å of N(10). The two planes makes an angle of 10.8°. The Ni···Ni distance in the dinuclear complex is 3.527(3) Å. Three types of coordination structures are hitherto known in monomethyl carbonato nickel(II) complexes.[3] However, the coordination structure of **1** and **2** is distinct from those for nickel(II) complexes reported by Kato and Ito.[3] Of course, to our knowledge, the dinuclear nickel(II) complex bridged by an alkoxo and a monomethyl carbonato has

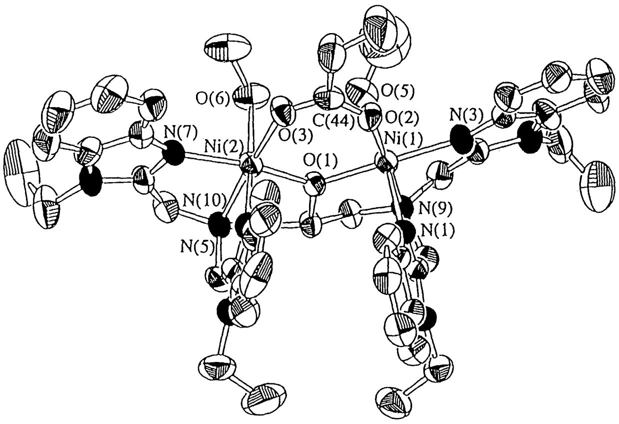

Figure 1. An ORTEP view of $[Ni_2(L)(OOC\text{-}O\text{-}CH_3)(CH_3OH)_2]^{2+}$. Selected bond lengths(Å) and angles(°): Ni(1)···Ni(2) 3.527(3), Ni(1)–O(1) 1.954(9), Ni(1)–O(2) 2.026(10), Ni(1)–O(5) 2.21(1), Ni(1)–N(1) 2.01(1), Ni(1)–N(3) 2.04(1), Ni(1)–N(9) 2.17(1), Ni(2)–O(1) 1.965(9), Ni(2)–O(3) 2.01(1), Ni(2)–O(6) 2.26(1), Ni(2)–N(5) 2.01(1), Ni(2)–N(7) 2.03(1), Ni(2)–N(10) 2.18(1), O(2)–C(44) 1.23(2), O(3)–C(44) 1.24(2) Å; Ni(1)–O(1)–Ni(2) 128.3(5), Ni(1)–O(2)–C(44) 131(1), O(1)–Ni(1)–O(2) 96.5(4), O(1)–Ni(1)–O(5) 81.4(4), O(1)–Ni(1)–N(1) 91.7(4), O(2)–Ni(1)–O(5) 86.8(4), O(2)–Ni(1)–N(1) 101.1(5), Ni(2)–O(3)–C(44) 131(1), O(1)–Ni(2)–O(3) 97.8(4), O(1)–Ni(2)–O(6) 82.9(4), O(1)–Ni(2)–N(5) 98.4(4), O(3)–Ni(2)–O(6) 84.8(4), O(3)–Ni(2)–N(5) 96.6(5), O(2)–C(44)–O(3) 131(1)°.

not been reported so far.

The magnetic moment of **2** at room temperature is 3.11 BM.[15] The data of temperature-dependence magnetic susceptibility of **2** show a peak near 40K, indicating an antiferromagnetic interaction between two nickel(II) ions. The magnetic parameters can be estimated as $g = 2.24$, $J = -17.6$ cm^{-1} ($H = -2J S_1 \cdot S_2$), and $N\alpha = 450$ cgs emu mol^{-1} from the best fit of the χ_A values to the equation (1).[16]

$$\chi_A = \frac{Ng^2\beta^2}{kT} \times \frac{5+\exp(4x)}{5+3\exp(4x)+\exp(6x)} + N\alpha \qquad (1)$$

where x, g, and $N\alpha$ are $-J/kT$ (J : the exchange integral), g factor, and T.I.P., respectively. The electronic absorption spectrum of **2** exhibits the d-d bands at 1012, 638, and 400 nm in a powder state, and at 1034 (ε, 13), 649 (ε, 20), and 410 nm (ε, 35 mol^{-1} dm^3 cm^{-1}) in *N,N*-dimethylformamide (DMF).[15] These J and λ_{max} values are similar to those ($J = -21.6$ cm^{-1} and λ_{max} = 1017, 644, and 407 nm in DMF) of $[Ni_2(L)(OAc)(H_2O)_2](ClO_4)_2$ bridged by an alkoxo and an acetato.[13]

In the same manner, the reaction of $[Ni_2(L)(OH)(H_2O)_2](ClO_4)_2$ (0.25 g, 0.23 mmol) with 1,1-dimethylurea or 1,3-dimethylurea (0.04 g, 0.46 mmol) was undertaken for obtaining further information on the reaction described above. As a result, dinuclear complex **2** having a similar elemental analyses (C, H, N, and Ni) and IR spectrum[17] was isolated from their reaction mixture. In addition, the structure of a single crystal obtained from the reaction solution containing 1,1-dimethylurea was also determined by X-ray crystallography, and it was the same compound as the complex **1**. On the other hand, the complex $Ni_2(L)$(*N*-methylurea)$(ClO_4)_3 \cdot H_2O \cdot 3CH_3OH$ has been isolated by a reaction of $[Ni_2(L)(OH)(H_2O)_2](ClO_4)_2$ with *N*-methylurea, and methanol under argon. From this result and the fact mentioned above,[6] it is clear that the monomethyl carbonato is produced by the reaction between methanol and dissolved CO_2 in the solution. Also, the complex **2** was not isolated from a reaction mixture of $[Ni_2(L)(OH)(H_2O)_2](ClO_4)_2$ and methanol in the absence of urea derivatives. From these results, it is suggested that *N*-methylurea, 1,1-dimethylurea or 1,3-dimethylurea does not react with $[Ni_2(L)(OH)(H_2O)_2](ClO_4)_2$, assisting the formation of monomethyl carbonato from methanol and CO_2. Studies on the role of urea derivatives and the mechanism for these reaction are now in progress.

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References and Notes

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5 Anal. Calcd for $C_{43}H_{54}N_{10}O_{12}Cl_2Ni_2$: C, 47.32; H, 5.00; N, 12.84. Found: C, 47.85; H, 5.01; N, 12.99.

6 Ammonia and *N*-methylamine were not detected during the reaction, showing that no hydrolysis of *N*-methylurea takes place. The detection of ammonia and *N*-methylamine was carried out by employing Nessler's reagent and ninhydrine solution, respectively.

7 Crystal data for **1**: F_w = 1227.41, triclinic, space group $P\bar{1}$, a = 15.984(7), b = 16.809(5), c = 12.549(4) Å, α = 101.77(3), β = 100.01(3), γ = 64.51(2)°, V = 2965(1) Å^3, Z = 2, D_m = 1.36 g cm^{-3}, D_c = 1.374 g cm^{-3}, μ(Mo$K\alpha$) = 7.96 cm^{-1}. A total of 10807 reflections with $2\theta < 50.0°$ was collected on a Rigaku AFC7R diffractometer using Mo$K\alpha$ radiation (λ = 0.71069 Å). Absorption correction was applied. The structure was solved by use of PATTY[8] and DIRDIF94[9] and refined by full-matrix least-squares to give R = 0.079 and R_w = 0.094 for 5508 observed reflections [$I > 3.00\sigma(I)$].[10] The maximum and minimum peaks on the final difference Fourier map were 0.76 and -0.52 eÅ^{-3}.

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11 Anal. of **2**. Calcd for $C_{45}H_{56}N_{10}O_{14}Cl_2Ni_2 \cdot H_2O$: C, 46.29; H, 5.02; N, 12.00, Ni, 10.05. Found: C, 46.57; H, 4.84; N, 12.22, Ni, 9.77.

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15 The magnetic moment and the absorption spectrum of **1** were not measured owing to a failure of the isolation as stable crystals in air.

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17 Anal. of the complex obtained from 1,1-dimethylurea. Found: C, 46.30; H, 4.83; N, 12.32; Ni, 9.83. Anal. of the complex obtained from 1,3-dimethylurea. Found: C,46.67; H,4.83; N,12.30; Ni, 10.32. The IR spectra of the Ni(II) complexes obtained from 1,1-dimethylurea and 1,3-dimethylurea agreed with that of **2**, respectively.