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A Novel μ-Carbonato-Bridged Binuclear Nickel(II) Complex with N,N′,N″,N‴-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane

Masahiro MIKURIYA,[*] Ichiro MURASE,[†] Eiji ASATO,[††] and Sigeo KIDA[††]
Department of Chemistry, School of Science, Kwansei Gakuin University,
Uegahara, Nishinomiya 662
[†]Laboratory of Chemistry, College of General Education, Kyushu University 01,
Ropponmatsu, Chuo-ku, Fukuoka 810
[††]Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki, Higashi-ku, Fukuoka 812

μ-Carbonato-bridged binuclear nickel(II) complexes with N,N′,N″,N‴-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec), $[Ni_2(taec)(CO_3)](ClO_4)_2 \cdot H_2O$ has been prepared and characterized by electronic spectra, magnetic susceptibilities (80–300 K), and X-ray structure analysis.

Metal complexes of tetraaza macrocycles with pendant arms on the nitrogen atoms have attracted much attention in the latest several years, since they showed specific complexation behavior, novel structures, unusual spectral and magnetic properties.[1-9] In the preceding papers,[6-9] we reported the synthesis and characterization of a series of metal complexes of N,N′,N″,N‴-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec). The taec ligand always forms 2:1 (metal:taec) binuclear metal complexes where each metal ion is coordinated by two cyclam ring nitrogens and two pendant amino nitrogens. So far, two types of binuclear structures are known for these complexes as shown in Fig. 1. In both cases

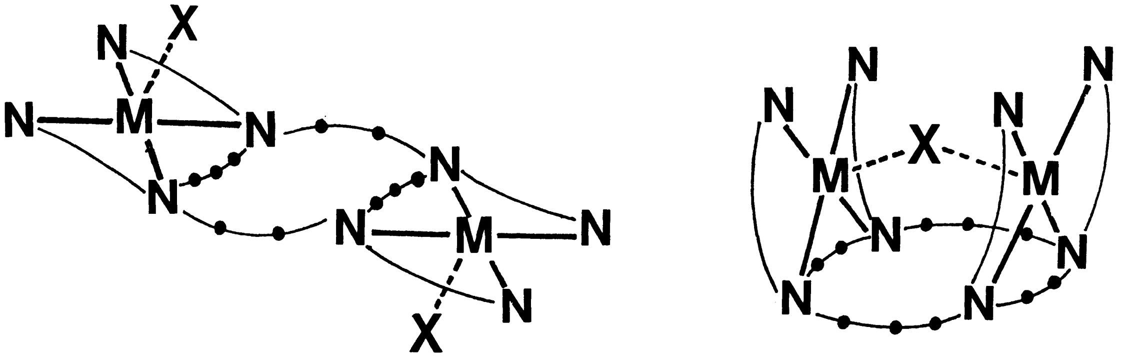

Fig. 1. Coordination modes of taec.

one of the axial sites is open for coordination on each metal ion, but the other site is blocked by the methylene groups of taec so that six-coordination is sterically hindered. This accounts for the fact that many attempts to isolate cobalt(III) taec complexes were all in vain.[6,9] However, during the course of our studies on metal complexes with taec, we have found that a six-coordinate structure can be achieved by the use of carbonate ion. Here we report the preparation and characterization of $[Ni_2(taec)(CO_3)](ClO_4)_2 \cdot H_2O$ (**1**) as the first example of six-coordinate metal complexes with taec.

The complex was prepared as follows. The ligand (taec•8HBr) was dissolved in a minimum amount of water. To this was added an excess of nickel(II) carbonate, and the mixture was heated on a water bath for 20 min. Insoluble material was filtered off, and sodium perchlorate was added to the filtrate. The pH of the solution was adjusted at 8-9 by the addition of sodium carbonate. The solution was concentrated to obtain blue crystals, which were collected and air-dried at room temperature.[10] The complex can be also prepared by adding sodium carbonate to an aqueous solution of $[Ni_2(taec)](ClO_4)_4$[6] at pH 8-9.

X-Ray structure analysis[11] revealed the binuclear structure with six-coordinate nickel ions linked by a carbonate ion in unique manner (Fig. 2). The $[Ni_2(taec)(CO_3)]^{2+}$ cation has a crystallographic mirror plane containing O1, C11, C1, and C6 atoms, and consequently the environments of the two nickel ions are identical. The taec ligand coordinates to both nickel ions with two cyclam ring nitrogens and two pendant amino nitrogens in a cis-β fashion and the carbonate ion acts

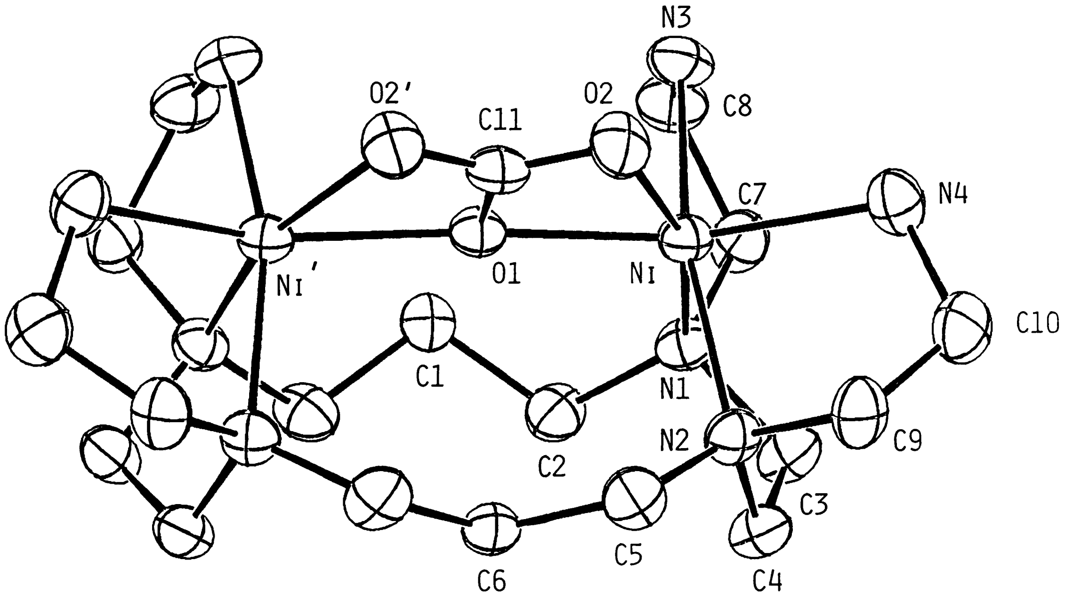

Fig. 2. Perspective view of $[Ni_2(taec)(CO_3)]^{2+}$. Selected bond lengths (l/Å) and angles (φ/°): Ni-Ni' 4.167(2), Ni-O1 2.086(9), Ni-O2 2.159(8), Ni-N1 2.112(8), Ni-N2 2.160(9), Ni-N3 2.106(10), Ni-N4 2.122(10); Ni-O1-Ni' 174.6(5), O1-Ni-O2 61.2(3).

as a symmetrical bidentate ligand to both nickel ions forming a distorted octahedron for each nickel ion. The Ni-N and Ni-O bond lengths (2.106(10)–2.160(9) Å and 2.086(9)–2.159(8) Å, respectively) are typical of those found in high-spin nickel(II) complexes with N_4 macrocyclic ligands.[3,7] The high-spin state of the nickel(II) ions was confirmed by electronic spectra. The electronic spectrum of (**1**) in water shows three d-d bands at 10.0×10^3 (ε = 16 $mol^{-1}dm^3cm^{-1}$/Ni), 16.8×10^3 (ε = 20 $mol^{-1}dm^3cm^{-1}$/Ni) and 26.7×10^3 cm^{-1} (ε = 33 $mol^{-1}dm^3cm^{-1}$/Ni). The bridging mode of the carbonate ion is novel for nickel(II), though this type of $Cu(\mu\text{-}CO_3)Cu$ bridge was found in $[LCu]_2(CO_3)(ClO_4)_2$ (**2**) (L = 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene)[12] and in $[(tmpd)CuCl]_2(CO_3)$ (**3**) (tmpd = N,N,N',N'-tetramethyl-1,3-propanediamine).[13] The magnetic moment per nickel ion (2.34 B.M. at room temperature) is considerably lower than those for high-spin nickel(II) complexes. Measurements of the magnetic susceptibilities in the range 80–300 K showed a ground state S = 0 (Fig. 3). The data could be analyzed by an isotropic Heisenberg model, $\mathcal{H} = -2JS_1\cdot S_2$ ($S_1 = S_2 = 1$). The solid curve in Fig. 3 was calculated by using the parameters, J = -75.8 cm^{-1} and g = 2.3 ($N\alpha$ = 0). To our knowledge this is the largest antiferromagnetic interaction among binuclear nickel(II) complexes so far reported except for those of copper(II) acetate type structure[14] and oximate bridge.[15] This is understandable, since the Ni-O1-Ni' angle (174.6(5)°) is close to 180°, and very strong antiferromagetic interaction via a carbonate ion was observed in the cases of the copper(II) complexes, (**2**) and (**3**). It is noteworthy that the octahedral structure has been attained by introducing a carbonate ion to form such a specific bridging structure. The present result suggests that the synthesis of cobalt(III) complexes with taec is promising. Such a study is now under way.

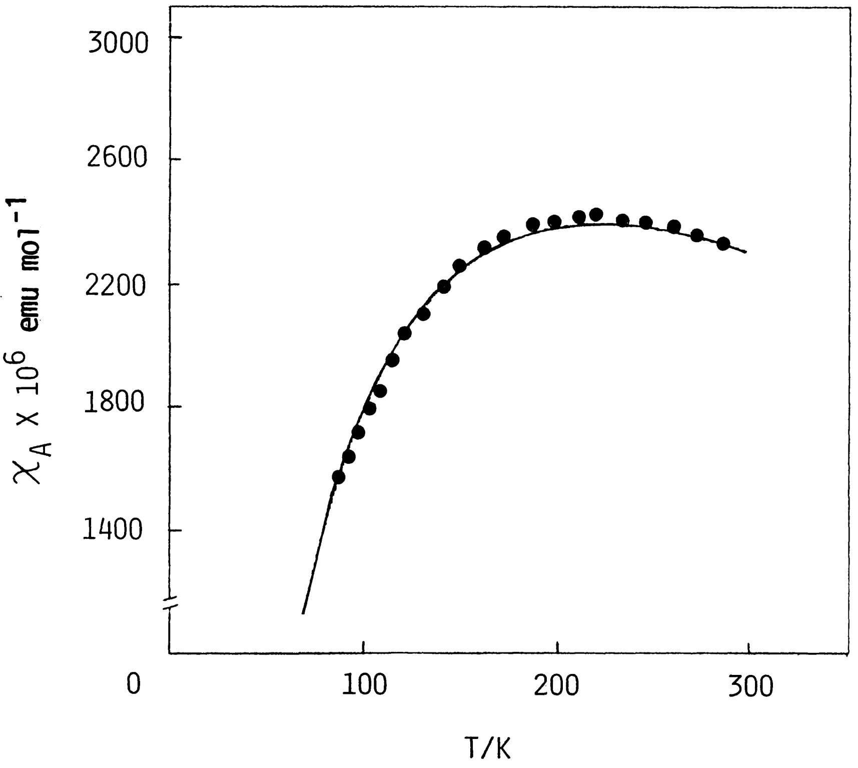

Fig. 3. Temperature dependence of magnetic susceptibilities of $[Ni_2(taec)(CO_3)](ClO_4)_2\cdot H_2O$.

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10) A satisfactory analysis (C, H, N) has been obtained.

11) Crystal data for (**1**): $C_{19}H_{46}Cl_2N_8Ni_2O_{12}$, orthorhombic, space group Pnnm, a = 17.319(2), b = 15.119(2), c = 13.040(2) Å, V = 3414.6(7) $Å^3$, Z = 4, D_c = 1.49 g cm^{-3}, μ(Mo-Kα) = 13.3 cm^{-1}, crystal dimensions 0.18×0.25×0.40 mm^3. Intensity data were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Mo-Kα radiation. A total of 5371 reflections (2θ < 60°) were obtained, of which independent 3104 reflections ($|F_o| > 3\sigma(F_o)$) were considered as observed. The structure was solved by the direct methods and refined by the block-diagonal least-squares method. The residual value was R = 0.111. All the calculations were carried out on the HITAC M-680H computer at the Computer Center of the Institute for Molecular Science using the UNICS-III programs.

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