Linkage Modes of Nickel(II) and Cobalt(III) Complexes with C-C Linked Bimacrocyclic Ligands

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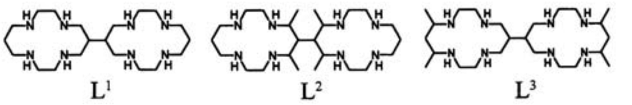
The X-ray structural analysis revealed three types of linkage modes (*eq-eq*, ax-eq, and *ax-ax*) due to the stereochemical difference in bridging two macrocycles by a C-C bond for bimacrocyclic nickel(II) and cobalt(III) complexes.

Many bimacrocyclic compounds where two macrocycles are linked by various functional groups have been reported.[1] Although the linkage by a C-C bond is a simple method, such a linkage has been known to afford new properties and interesting structures, which are never observed in the corresponding monomacrocyclic one. For example, the nickel(II) complex with L^1 has been reported as a more effective catalyst for the reduction of water to hydrogen compared with the corresponding monomacrocyclic nickel(II) complex, $[Ni(cyclam)]^{2+}$.[2] We also reported that the nickel(II) complex with L^2 shows higher catalytic activity in the photochemical reduction of CO_2 than the corresponding monomacrocyclic nickel(II) complex, as well as an interesting dimeric structure bearing unusual 1,3-diaxial methyl substituents.[1] In the nickel(II)[1] and cobalt(III)[3] complexes with L^2, only the complex with the equatorial-equatorial (*eq-eq*) C-C linkage, where both macrocycles were linked equatorially with respect to the six-membered chelate ring, was isolated, though three complexes with *eq-eq*, *ax-eq* (axial-equatorial), and *ax-ax* (axial-axial) C-C linkage modes between two macrocycles could be proposed (see Figures 1 and 2). In the present study, we succeeded in revealing for the first time three different C-C linkage modes between two macrocycles by the X-ray structural analysis of new nickel(II) complexes with L^3, which is a geometrical isomer of the ligand L^2, and cobalt(III) complexes with L^1, which does not have methyl substituents.



New nickel(II) complexes with L^3 were synthesized as follows. The oxidation of 5*R*(*S*),7*S*(*R*)-dimethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) perchlorate with 30% hydrogen peroxide in 1 mol dm^{-3} $HClO_4$ at 60 °C yielded the deep violet dimer of the starting complex, bis[5*R*(*S*),7*S*(*R*)-dimethyl-1,4,8,11-tetraaza-11,14-cyclotetradecadien-13-ylidenenickel(II)] perchlorate.[4] The five double bonds in the dimer were reduced with $NaBH_4$ to produce the mixture of *eq-eq*[5] and *ax-eq*[6] nickel(II) complexes with the saturated ligand L^3. The complexes, which did not show isomerization in aqueous solution, were separated by column chromatography using SP Sephadex C-25 and isolated as perchlorates (yield ratio: *eq-eq* : *ax-eq* = ca. 3 : 1).[5,6] The FAB-mass spectra of both perchlorates showed the peaks with the same isotropic distribution pattern at m/z 869 for $[M\text{-}ClO_4]^+$, confirming that they are isomers with respect to the complex cations.

Perchlorates of the nickel(II) complexes were converted to the azide and the iodide salts in order to produce crystals for the X-ray structural analysis, which clearly confirmed the difference in the C-C linkage mode between the two macrocycles.[7] The structures of $[Ni_2(\textit{eq-eq}\text{-}L^3)(N_3)_4]$[8] and $[Ni_2(\textit{ax-eq}\text{-}L^3)(OH_2)]^{4+}$ [9] are shown in Figure 1. In $[Ni^2(\textit{eq-eq}\text{-}L^3)(N_3)_4]$, two macrocycles are equatorially linked by the C-C bond at both the 13- and 13' -positions with respect to the six-membered chelate rings and separated as far as possible; the nickel(II)-nickel(II) distance is 8.181 Å. The two macrocycles adopt the *trans*-III[10] N_4 configuration containing the six-coordinate nickel(II) associated with azide ions. They are twisted by ca. 60° around the C(13)-C(13') bond probably to avoid the steric repulsion between the coordinated azide ions. The average bond length of $Ni\text{-}N_4$ is 2.076 Å, which is a typical value for the high-spin six-coordinate nickel(II) in macrocyclic lig-

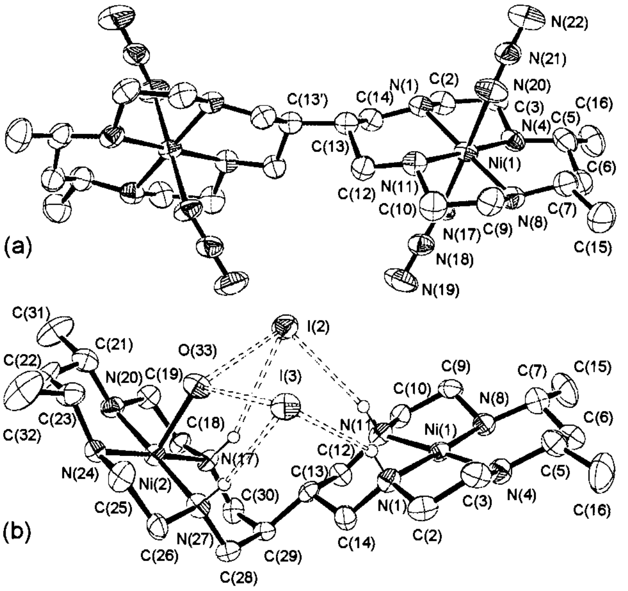


Figure 1. ORTEP drawing for the cations of $[Ni_2(\textit{eq-eq}\text{-}L^3)(N_3)_4]\cdot 2H_2O$ (a) and $[Ni_2(\textit{ax-eq}\text{-}L^3)(H_2O)]I_4$ (b). Selected bond distances (Å) and bond angles (°) of (a): Ni(1)-N(4) 2.075(3), Ni(1)-N(8) 2.075(3), Ni(1)-N(11) 2.075(3), Ni(1)-N(1) 2.077(3), Ni(1)-N(20) 2.140(3), Ni(1)-N(17) 2.165(3), C(13)-C(13') 1.556(6), N(4)-Ni(1)-N(8) 96.28(11), N(8)-Ni(1)-N(11) 85.50(11), N(4)-Ni(1)-N(1) 85.56(11), N(11)-Ni(1)-N(1) 92.68(10), N(4)-Ni(1)-N(20) 95.08(12), N(1)-Ni(1)-N(20) 88.91(12), N(4)-Ni(1)-N(17) 84.41(11), N(1)-Ni(1)-N(17) 90.01(12), N(20)-Ni(1)-N(17) 178.83(13), and (b): Ni(2)-N(27) 2.050(6), Ni(2)-N(17) 2.057(6), Ni(2)-N(24) 2.084(7), Ni(2)-N(20) 2.095(7), Ni(2)-O(33) 2.147(6), Ni(1)-N(11) 1.923(7), Ni(1)-N(4) 1.944(7), Ni(1)-N(1) 1.952(7), Ni(1)-N(8) 1.957(7), C(13)-C(29) 1.557(11), N(27)-Ni(2)-N(17) 94.4(2), N(27)-Ni(2)-N(24) 85.5(3), N(17)-Ni(2)-N(20) 84.9(3), N(24)-Ni(2)-N(20) 95.1(3), N(17)-Ni(2)-O(33) 91.4(3), N(20)-Ni(2)-O(33) 91.5(3), N(11)-Ni(1)-N(1) 90.2(3), N(4)-Ni(1)-N(1) 87.4(3), N(11)-Ni(1)-N(8) 86.7(3), N(4)-Ni(1)-N(8) 95.8(3), I(2)---N(11) 3.685, I(2)---N(17) 3.980, I(2)---O(33) 3.387, I(3)---N(1) 3.665, I(3)---N(27) 3.870, I(3)---O(33) 3.466.

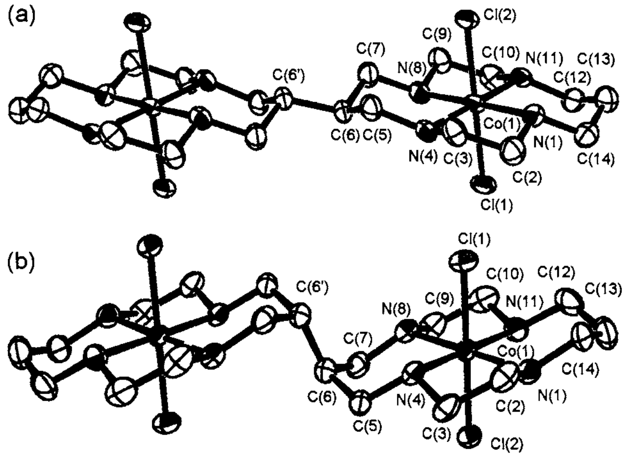


Figure 2. ORTEP drawing for the cations of $[Co_2(\textit{eq-eq}\text{-}L^1)Cl_4]Cl_2\cdot 6H_2O$ (a) and $[Co_2(\textit{ax-ax}\text{-}L^1)Cl_4]Cl_2\cdot 4H_2O$ (b). Selected bond distances (Å) and bond angles (°) of (a): Co(1)-N(8) 1.963(5), Co(1)-N(4) 1.976(6), Co(1)-N(11) 1.976(6), Co(1)-N(1) 1.980(5), Co(1)-Cl(2) 2.253(2), Co(1)-Cl(1) 2.258(2), C(6)-C(6') 1.559(11), N(8)-Co(1)-N(4) 93.5(2), N(8)-Co(1)-N(11) 85.8(2), N(4)-Co(1)-N(1) 85.8(2), N(11)-Co(1)-N(1) 94.9(2), N(4)-Co(1)-Cl(2) 88.5(2), N(1)-Co(1)-Cl(2) 91.0(2), N(4)-Co(1)-Cl(1) 91.8(2), N(1)-Co(1)-Cl(1) 89.1(2), and (b): Co(1)-N(8) 1.972(5), Co(1)-N(11) 1.978(5), Co(1)-N(4) 1.981(5), Co(1)-N(1) 1.984(5), Co(1)-Cl(1) 2.249(2), Co(1)-Cl(2) 2.267(2), C(6)-C(6') 1.539(12), N(8)-Co(1)-N(11) 85.9(2), N(8)-Co(1)-N(4) 93.1(2), N(11)-Co(1)-N(1) 95.1(2), N(4)-Co(1)-N(1) 85.9(2), N(4)-Co(1)-Cl(1) 91.5(2), N(1)-Co(1)-Cl(1) 87.7(2), N(4)-Co(1)-Cl(2) 88.8(2), N(1)-Co(1)-Cl(2) 92.3(2).

ands.[10] On the other hand, in $[Ni_2(\textit{ax-eq}\text{-}L^3)(H_2O)]I_4$, one macrocycle is axially linked by the C-C bond at the 29-position and the other one is equatorially linked at the 13-position with respect to the six-membered chelate rings. Because of this linkage mode, the molecular shape is bent like a half-opened clamshell that forms two kinds of nickel(II) ions with different coordination geometries. Although both macrocycles adopt the *trans*-III N_4 configuration, one nickel(II) in the equatorially linked macrocycle takes the four-coordination geometry (av. Ni-N_4 = 1.944 Å) and the other one has the five-coordination[11] geometry (av. Ni-N_4 = 2.072 Å). The nickel(II)-nickel(II) distance is 7.073 Å, which is considerably shorter than that of the above *eq-eq* complex. Such a half-opened clamshell shape seems to afford the *ax-eq*-linked complex, a new interesting function incorporating anions between two macrocycles. Two iodide ions are closely trapped between the two macrocycles by hydrogen bonds formed with the secondary amine protons and the coordinated water molecule, as shown in Figure 1b.

The *eq-eq* and *ax-ax* linkage modes were found in the cobalt(III) complex with L^1. The reaction of $CoCl_2\cdot 6H_2O$ with L^1 [12] in methanol followed by aerial oxidation gave a crude green product of the cobalt(III) complex with L^1, which was purified by SP Sephadex C-25 columm chromatography (0.4 mol dm^{-3} NaCl). After the removal of NaCl, the obtained green crystals were further recrystallized from 1 mol dm^{-3} HCl to give three kinds of crystals. The X-ray crystallography has revealed that two of them are the *eq-eq* and *ax-ax* linked complexes (Figure 2).[13] Two complex cations, $[Co_2(\textit{eq-eq}\text{-}L^1)Cl_4]^{2+}$ [14] and $[Co_2(\textit{ax-ax}\text{-}L^1)Cl_4]^{2+}$,[15] are in the isomerism due to the difference in the C-C linkage mode between the two macrocycles. Each macrocycle adopts the *trans*-III N_4 configuration and all the cobalt(III) ions are in the six-coordination geometry with chloride ions in either complex. The cobalt(III)-cobalt(III) distance is considerably shorter in $[Co_2(\textit{ax-ax}\text{-}L^1)Cl_4]^{2+}$ (7.391 Å) than in $[Co_2(\textit{eq-eq}\text{-}L^1)Cl_4]^{2+}$ (8.259 Å), because of the difference in the C-C linkage mode.

Thus, L^1 and L^3, which have no methyl substituents around the C-C brigde, enabled us to reveal the presence of *eq-eq*, *ax-eq*, and *ax-ax* linkage modes between two macrocycles for the C-C linked bimacrocyclic complexes. Detailed studies on the differences in the physical properties are now in progress.

References and Notes

1 K. Mochizuki, S. Manaka, I. Takeda, and T. Kondo, *Inorg. Chem.*, **35**, 5132 (1996) and references therein.

2 J. -P. Collin, A. Jovaiti, and J. -P. Sauvage, *Inorg. Chem.*, **27**, 1986 (1986).

3 K. Mochizuki, K. Ikeuchi, and T. Kondo, *Bull. Chem. Soc. Jpn.*, **71**, 2629 (1998).

4 FAB-Mass: m/z 859 for $[M\text{-}ClO_4]^+$. Details will be reported elsewhere.

5 $[Ni_2(\textit{eq-eq}\text{-}L^3)](ClO_4)_4$: Anal. Found: C: 29.99, H: 5.68, N: 11.55%. Calcd for $C_{24}H_{54}N_8Ni_2Cl_4O_{16}$: C: 29.81, H: 5.63, N: 11.60%. FAB-Mass: m/z 869 for $[M\text{-}ClO_4]^+$.

6 $[Ni_2(\textit{ax-eq}\text{-}L^3)](ClO_4)_4\cdot H2O$: Anal. Found: C: 29.20, H: 5.47, N: 11.12%. Calcd for $C_{24}H_{56}N_8Ni_2Cl_4O_{17}$: C: 29.26, H: 5.73, N: 11.38%. FAB-Mass: m/z 869 for $[M\text{-}ClO_4]^+$.

7 The azide (iodide) was easily derived from the addition of NaN_3 (NaI) to an aqueous solution of the chloride of the nickel(II) complex, which was prepared prior to passing the perchlorate through a Cl-form anion-exchange resin. Crystals of the triflate for the *ax-eq* nickel(II) complex and the iodide and the perchlorate for the *eq-eq* nickel(II) complex were also obtained, though their qualities of the X-ray analysis were not sufficient.

8 $[Ni_2(\textit{eq-eq}\text{-}L^3)(N_3)_4]\cdot 2H_2O$: $C_{24}H_{58}N_{20}Ni_2O_2$; FW = 776.24; T = 298(2) K; Mo Kα 0.71073 Å; Monoclinic; *C*2/*c*; *a* = 21.096(5) Å, *b* =7.949(3) Å, *c* = 21.788(5) Å; β =102.51(2)° ; V = 3567(2) Å^3; Z = 4; D_{calcd} = 1.446 Mg/m^3; D_{meas} = 1.439 Mg/m^3; μ = 1.111 mm^{-1}; *F*(000) = 1656; (0.47 x 0.40 x 0.20 mm); Mac Science MXC3k; 1.91 ≦ θ ≦ 27.61° ; Independent reflections: 4127 (R_{int} = 0.019); Full-matrix least-squares on F^2; Data / restraints / parameters: 4127 (2890) / 0 / 217; Goodness-of-fit on F^2: 1.031: Final R [$I > 2\sigma(I)$]: R_1 = 0.0456, wR_2 = 0.1101; *R* (all data): R_1 = 0.0777, wR_2 = 0.1293; Largest diff. peak and hole: 0.512 and -0.430 eÅ^3.

9 $[Ni_2(\textit{ax-eq}\text{-}L^3)(H_2O)]I_4$: $C_{24}H_{58}I_4Ni_2O$; FW = 1097.76; T = 298(2) K; Mo Kα 0.71073 Å; Monoclinic; *P*2$_1$/*c*; *a* = 18.203(3) Å, *b* = 13.423(2) Å, *c* = 16.127(3) Å; β = 111.92(2)° ; V = 3655.5(12) Å^3; Z = 4; D_{calcd} = 1.995 Mg/m^3; D_{meas} = 1.991 Mg/m^3; μ = 4.438 mm^{-1}; *F*(000) = 2128; (0.50 x 0.25 x 0.05 mm); Mac Science MXC3k; 1.91 ≦ θ ≦ 27.51° ; Independent reflections: 8396 (R_{int} = 0.023); Full-matrix least-squares on F^2; Data / restraints / parameters: 8396 (6107) / 0 /352; Goodness-of-fit on F^2: 1.018: Final *R* [$I > 2\sigma(I)$]: R_1 = 0.0725, wR_2 = 0.1767; *R* (all data): R_1 = 0.0977, wR_2 = 0.1955; Largest diff. peak and hole: 2.977 and -2.600 eÅ^3.

10 "Coordination Chemistry of Macrocyclic Compounds," ed by G. A. Melson, Plenum Press, New York (1979).

11 Although one iodide is located near Ni(2), we tentatively assigned Ni(2) to the five-coordinate species because the distance (Ni(2)-I(1) = 3.0356(13) Å) is too long and the position of the iodide is not suitable for coordination to the nickel(II) ion (N(24)-Ni(2)-I(1) 83.7(2), N(20)-Ni(2)-I(1) 85.5(2), O(33)-Ni(2)-I(1) 173.3(2)).

12 L. Fabbrizzi, L. Montagna, A. Poggi, T. A. Kaden, and L. C. Siegfried, *J. Chem. Soc., Dalton Trans.* **1987**, 2631.

13 The *ax-eq* isomer was also isolated but the quality of the X-ray analysis was not sufficient: Preliminary crystal data: *a* = 14.586(3) Å, *b* = 34.545(7) Å, *c* = 7.501(2) Å; *V* = 3779.5(14) Å^3; Orthorhombic.

14 $[Co_2(\textit{eq-eq}\text{-}L^1)Cl_4]Cl_2\cdot 6H_2O$: $C_{20}C_{16}Co_2H_{58}N_8O_6$; FW = 837.31; T = 298(2) K; Mo Kα 0.71073 Å; Triclinic; *P* 1 ; *a* = 6.3080(9) Å, *b* = 9.227(4) Å, *c* = 15.849(3) Å; α = 86.78(3)° ; β = 79.362(13)° ; γ = 76.06(2)° ; *V* = 879.8(4) Å^3; *Z* = 1; D_{calcd} = 1.580 Mg/m^3; μ = 1.444 mm^{-1}; *F*(000) = 438; (0.35 x 0.30 x 0.25 mm); Mac Science MXC3k; 2.27 ≦ θ ≦ 27.50°; Independent reflections: 4030 (R_{int} = 0.009); Full-matrix least-squares on F^2; Data / restraints / parameters: 4030 (2247) / 0 /193; Goodness-of-fit on F^2: 1.129: Final *R* [$I > 2\sigma(I)$]: R_1 = 0.0599, wR_2 = 0.1506; *R* (all data): R_1 = 0.1340, wR_2 = 0.2204; Largest diff. peak and hole: 1.440 and -0.809 eÅ^3.

15 $[Co_2(\textit{ax-ax}\text{-}L^1)Cl_4]Cl_2\cdot 4H_2O$: $C_{20}C_{16}Co_2H_{54}N_8O_4$; FW = 801.28; T = 298(2) K; Mo Kα 0.71073 Å; Monoclinic; *P*2$_1$/*n*; *a* = 14.319(3) Å, *b* = 10.860(2) Å, *c* = 11.301(3) Å; β = 107.73(2)° ; *V* = 1673.9(6) Å^3; *Z* = 2; D_{calcd} = 1.590 Mg/m^3; μ = 1.510 mm^{-1}; *F*(000) = 836; (0.45 x 0.40 x 0.40 mm); Mac Science MXC3k; 2.02 ≦ θ ≦ 27.52°; Independent reflections: 3859 (R_{int} = 0.036); Full-matrix least-squares on F^2; Data / restraints / parameters: 3859 (2658) / 0 /181; Goodness-of-fit on F^2: 1.125: Final *R* [$I > 2\sigma(I)$]: R_1 = 0.0630, wR_2 = 0.1637; *R* (all data): R_1 = 0.1063, wR_2 = 0.2166; Largest diff. peak and hole: 1.072 and -0.954 eÅ^3.