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Synthesis and Structure of [6,6′-Bi(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane)]dinickel(II) Triflate and Its Catalytic Activity for Photochemical CO_2 Reduction

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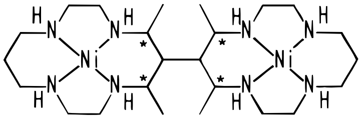
A new bimacrocyclic Ni(II) complex, [6,6′-bi(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane)]dinickel(II) triflate, was synthesized and its structure was determined by X-ray crystallography ($C_{28}H_{54}N_8Ni_2F_{12}S_4O_{12}$, monoclinic space group $P2_1/a$, $a = 15.282(2)$ Å, $b = 16.967(2)$ Å, $c = 9.172(1)$ Å, $\beta = 94.01(1)°$, $Z = 2$). Two dimethylcyclam units in the *trans III* form are linked equatorially with respect to the chair-form six-membered chelate ring, and the chirality due to a pair of asymmetric carbons in both macrocycles is C*-*meso* (5*R*(*S*), 7*S*(*R*)). The most remarkable feature, different from the case of corresponding monocyclic complex, is the configuration of methyl groups which occupy the axial positions of the six-membered chelate rings. Such a dimeric structure reduces the capability for accepting axially coordinating water molecules. On the other hand, the catalytic activity of the bimacrocyclic complex significantly exceeds that of the monocyclic Ni(II) complexes for photochemical CO_2 reduction.

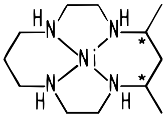
Introduction

Bimacrocyclic metal complexes having two linked macrocycles are of great interest, because they are good models for polynuclear metalloenzyme and multielectron redox catalysts. Such a situation has led to the syntheses of a number of bimacrocyclic complexes with a variety of bridges.[1−7] Bimacrocyclic metal complexes often show interesting features different from those of monocyclic compounds. For example, it has been reported that the binuclear Cu(II) complex with bi(dioxocyclam)[1] having two 14-membered rings linked by a C−C bond shows two septulets in the ESR spectrum and a stepwise oxidation of Cu(II) ions in the differential polarogram, which are never observed for monomacrocyclic complexes; they are due to weak metal−metal interactions because of the proximate location of two Cu(II) ions. It has been also reported that the binuclear Ni(II) complex with bicyclam,[2] which is a reduction product of the bi(dioxocyclam), acts as a better catalyst than the monocyclic cyclam−Ni(II) complex, in hydrogen generation by the electrochemical reduction of water.[8,9] Thus, it is very interesting to discover the remarkable differences between bimacrocyclic metal complexes and monomacrocyclic metal complexes and to clarify how bimacrocyclic effects appear.

In the present study, we have synthesized a new bimacrocyclic Ni(II) complex, [6,6′-bi(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane)]dinickel(II) triflate, **1**(CF_3SO_3)$_4$, and compared its structure, solution behavior, and catalytic properties with those of the corresponding monomacrocyclic Ni(II) complex, **2**. The new bimacrocyclic complex **1** has been found to show surprising features different from those of the corresponding monocyclic one, **2**, although the two dimethylcyclam units are simply linked by a C−C bridge.



1 *(meso-meso)*



2 *(meso)*

Results and Discussion

Synthesis of the Bimacrocyclic Dinickel(II) complex 1(CF_3-SO_3)$_4$. In the case of the previously reported bimacrocycle **3** having a C−C bridge, the C−C bridge was introduced by organic synthesis before the complex formation.[2] We took

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[1] Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Seghi, B. *J. Chem. Soc., Chem. Commun.* **1982**, 1166. Fabbrizzi, L.; Forlini, F.; Perotti, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 807. Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 3917.

[2] Fabbrizzi, L.; Montagna, L.; Poggi, A.; Kaden, T. A.; Siegfried, L. C. *Inorg. Chem.* **1986**, *25*, 2671. Fabbrizzi, L.; Montagna, L.; Poggi, A.; Kaden, T. A.; Siegfried, L. C. *J. Chem. Soc., Dalton Trans.* **1987**, 2631.

[3] Barefield, E. K.; Chueng, D.; Van Deveer, D. G.; Wagner, F. *J. Chem. Soc., Chem. Commun.* **1981**, 302. Foster, K. A.; Brown, D. R.; Timken, M. D.; Van Derveer, D. G.; Belford, R. L.; Barefield, E. K. *J. Coord. Chem.* **1988**, *19*, 123.

[4] Murase, I.; Hamada, K.; Kida, S. *Inorg. Chim. Acta* **1981**, *54*, L171. Murase, I.; Hamada, K.; Ueno, S.; Kida, S. *Synth. React. Inorg. Met.-Org. Chem.* **1983**, *13*, 191. Murase, I.; Ueno, S.; Kida, S. *Inorg. Chim. Acta* **1986**, *111*, 57.

[5] Mochizuki, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1023. Mochizuki, K.; Endoh, Y. *Bull. Chem. Soc. Jpn.*, **1989**, *62*, 936. Mochizuki, K.; Ikeda, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1587. Mochizuki, K.; Iijima, A.; Endoh, Y.; Ikeda, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 565. Mochizuki, K.; Tsutsumi, M.; Yamaji, Y. *Inorg. Chim. Acta* **1992**, *191*, 35. Mochizuki, K.; Lu, H. Y.; Suzuki, Y. *Inorg. Chim. Acta* **1993**, *204*, 267. Mochizuki, K.; Higashiya, S.; Uyama, M.; Kimura, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2673.

[6] Schneider, R.; Riesen, A.; Kaden, T. A. *Helv. Chim. Acta* **1985**, *68*, 53. Urfer, A.; Kaden, T. A. *Helv. Chim. Acta* **1994**, *77*, 23. Comba, P.; Hilfenhaus, P. *J. Chem. Soc., Dalton Trans.* **1995**, 3269. Kajiwara, T.; Yamaguchi, T.; Kido, H.; Kawabara, S.; Kuroda, R.; Ito, T. *Inorg. Chem.* **1993**, *32*, 4990. Ciampolini, M.; Micheloni, M.; Nardi, N.; Vizza, F.; Buttafava, A.; Fabbrizzi, L.; Perotti, A. *J. Chem. Soc., Chem. Commun.* **1984**, 998. Ciampolini, M.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Seghi, B.; Zanobini, F. *Inorg. Chem.* **1987**, *26*, 3527.

[7] Spreer, L. O.; Allen, C. B.; MacQueen, D. B.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1994**, *116*, 2187. Mountford, H. S.; MacQueen, D. B.; Li, A.; Otvos, J. W.; Calvin, M.; Frankel, R. B.; Spreer, L. O. *Inorg. Chem.* **1994**, *33*, 1748. McAuley, A.; Xu, C. *Inorg. Chem.* **1992**, *31*, 5549.

[8] Collin, J.-P.; Jouaiti, A.; Sauvage, J.-P. *Inorg. Chem.* **1988**, *27*, 1986.

[9] Mochizuki, K.; Goto, H.; Suwabe, M.; Sakakibara, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1750.

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Scheme 1

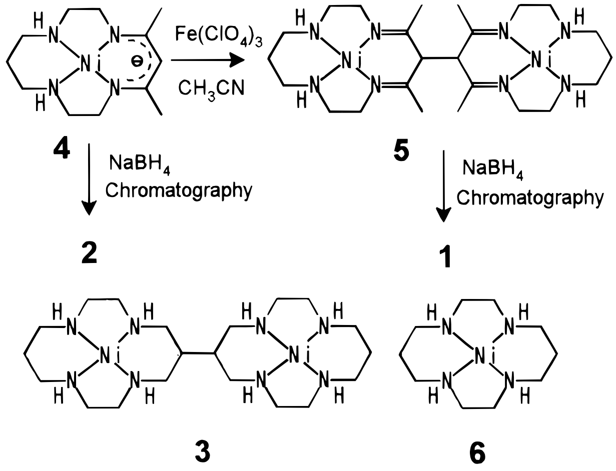

Table 1. Crystallographic Data for **1**(CF_3SO_3)$_4$

empirical formula	$C_{28}H_{54}N_8Ni_2F_{12}S_4O_{12}$	Z	2
fw	1168.38	ρ_{obsd}, g cm^{-3}	1.62
crystal system	monoclinic	ρ_{calcd}, g cm^{-3}	1.64
space group	$P2_1/a$	λ, Å	0.710 73
a, Å	15.282(2)		(Mo Kα)
b, Å	16.967(2)	T, °C	25
c, Å	9.172(1)	μ, cm^{-1}	10.71
β, deg	94.01(1)	R^a	0.059
V, Å^3	2372.5(5)	R_w^b	0.054

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2|/\Sigma w|F_o|^2\}$; $w = \exp(10.0(\sin^2\theta)/\lambda^2)/\sigma^2(F_o)$.

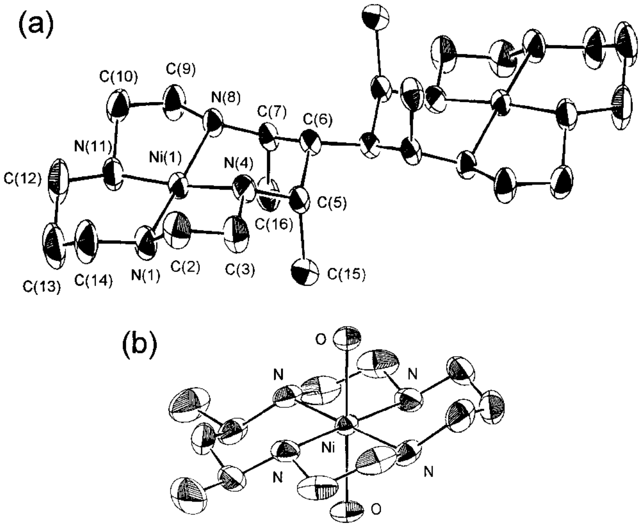

Figure 1. Perspective views of the complex cation in **1**(CF_3SO_3)$_4$ and [**2**(OH_2)$_2$]Cl_2·2H_2O (from ref 12).

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso),[a] Å^2
Ni(1)	0.20542(3)	0.09424(3)	0.78383(6)	0.031
N(1)	0.2681(3)	0.1931(2)	0.8094(5)	0.044
N(4)	0.1654(2)	0.1116(2)	0.9769(4)	0.033
N(8)	0.1492(2)	−0.0078(2)	0.7771(3)	0.032
N(11)	0.2488(3)	0.0673(2)	0.5958(4)	0.041
C(2)	0.2843(3)	0.2046(3)	0.9694(6)	0.050
C(3)	0.1979(4)	0.1896(3)	1.0338(6)	0.049
C(5)	0.0708(2)	0.0977(2)	1.0073(3)	0.031
C(6)	0.0465(2)	0.0105(2)	0.9746(3)	0.028
C(7)	0.0556(3)	−0.0161(2)	0.8151(4)	0.030
C(9)	0.1647(3)	−0.0488(3)	0.6366(5)	0.044
C(10)	0.2522(3)	−0.0204(3)	0.5920(6)	0.046
C(12)	0.3337(4)	0.1001(4)	0.5497(8)	0.068
C(13)	0.3381(5)	0.1880(4)	0.5732(9)	0.075
C(14)	0.3496(4)	0.2085(3)	0.7325(8)	0.063
C(15)	0.0103(3)	0.1597(3)	0.9341(6)	0.044
C(16)	−0.0075(3)	0.0209(3)	0.7016(4)	0.041
C(17)	0.0878(6)	0.2975(3)	0.3713(9)	0.075
C(18)	0.3992(6)	−0.0555(7)	1.1309(17)	0.115
S(1)	0.06711(9)	0.20008(7)	0.44787(15)	0.050
S(2)	0.28349(9)	−0.07431(8)	1.14353(15)	0.051
F(1)	0.1711(4)	0.3128(3)	0.3818(10)	0.150
F(2)	0.0454(4)	0.3529(2)	0.4341(7)	0.109
F(3)	0.0632(6)	0.2993(4)	0.2332(6)	0.148
F(4)	0.4373(4)	−0.0342(5)	1.2493(12)	0.182
F(5)	0.4392(4)	−0.1178(5)	1.0849(10)	0.168
F(6)	0.4062(6)	0.0012(6)	1.0312(13)	0.225
O(1)	0.1263(3)	0.1492(2)	0.3762(5)	0.062
O(2)	−0.0217(3)	0.1868(3)	0.4104(8)	0.098
O(3)	0.0910(5)	0.2099(3)	0.5997(5)	0.091
O(4)	0.2526(4)	−0.0970(3)	1.0001(6)	0.083
O(5)	0.2824(5)	−0.1371(3)	1.2480(6)	0.090
O(6)	0.2515(3)	0.0001(3)	1.1915(5)	0.071

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

advantage of the high reactivity of the sixth position of the (5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-dienato)nickel(II) ion, **4**, to synthesize bimacrocyclic Ni(II) complexes. Complex **4** in acetonitrile shows an irreversible anodic wave at +0.64 V *vs* SCE in its cyclic voltammogram; this is due to the radical formation at the sixth position of the six-membered chelate ring of the complex.[10] For the oxidation of the complex, we used Fe(III) ion ($Fe(ClO_4)_3$·6H_2O ($E_{1/2}^{II/III} = +1.1$ V *vs* SCE in CH_3CN)[11]). The synthesis of the bimacrocyclic dinickel(II) complex, **1**(CF_3SO_3)$_4$, is shown in Scheme 1. Complex **4** was oxidized by Fe(III) ions in N_2-purged acetonitrile, which caused a radical coupling reaction and readily produced a bimacrocyclic Ni(II) complex having four C=N bonds, **5**. Then the C=N bonds were reduced with $NaBH_4$ to yield a saturated product according to our previously reported method.[12] Because the reduction product was assumed to be a mixture of several isomers due to the difference in the chirality of the asymmetric carbons formed by the reduction, the reduced complexes were separated by column chromatography using the cation-exchange resin SP-Sephadex C-25. Three bands were eluted during the chromatography, of which the last main band was collected and isolated as the perchlorate, which was then converted to the triflate. The ^{13}C NMR spectrum of the isolated triflate in CD_3NO_2 shows one methyl, four methylene, and two methine signals, suggesting the presence of only one isomer in which two macrocycles are pairwise equivalent. This was confirmed as the *meso*−*meso* isomer, in which two C*-*meso* macrocycles are linked, using the following X-ray crystallography.

Structure of the Dimeric Ni(II) Complex 1(CF_3SO_3)$_4$. Figure 1a shows the X-ray structure of isolated dimeric nickel complex **1**. Crystal data and experimental details, fractional atomic coordinates, and selected bond lengths and angles are listed in Tables 1−3, respectively. Two dimethylcyclam units are actually linked equatorially with respect to the chair-form six-membered chelate ring by a C−C single bond at the sixth positions of the chelate rings; an inversion center exists at the midpoint of the C−C bridge. The macrocyclic skeleton is the

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(10) Mochizuki, K.; Toriumi, K.; Ito, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 881.

(11) Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 1852.

(12) Kondo, T.; Mochizuki, K. Presented at the 68th Annual Meeting of the Chemical Society of Japan, Nagoya, Oct 1, 1994; see Abstracts, p 187. Mochizuki, K.; Kondo, T.; Manaka, S.; Kajiwara, T.; Ito, T. *J. Coord. Chem.* **1996**, *37*, 205.

Table 3. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations

Ni(1)−N(1)	1.937(4)	Ni(1)−N(4)	1.936(4)
Ni(1)−N(8)	1.931(4)	Ni(1)−N(11)	1.945(4)
N(1)−C(2)	1.484(8)	N(1)−C(14)	1.496(8)
N(4)−C(3)	1.494(6)	N(4)−C(5)	1.509(5)
N(8)−C(7)	1.502(6)	N(8)−C(9)	1.499(6)
N(11)−C(10)	1.491(7)	N(11)−C(12)	1.499(8)
C(2)−C(3)	1.506(8)	C(5)−C(6)	1.549(6)
C(5)−C(15)	1.526(6)	C(6)−C(6′)	1.567(5)
C(6)−C(7)	1.546(5)	C(16)−C(7)	1.506(6)
C(10)−C(9)	1.504(7)	C(12)−C(13)	1.508(11)
C(14)−C(13)	1.500(11)		

N(4)−Ni(1)−N(8)	89.9(2)	N(4)−Ni(1)−N(11)	174.8(2)
N(4)−Ni(1)−N(1)	86.7(2)	N(8)−Ni(1)−N(11)	86.5(2)
N(8)−Ni(1)−N(1)	174.1(2)	N(11)−Ni(1)−N(1)	96.5(2)
Ni(1)−N(1)−C(2)	106.3(3)	Ni(1)−N(1)−C(14)	121.0(4)
C(2)−N(1)−C(14)	110.9(5)	Ni(1)−N(4)−C(5)	120.9(3)
Ni(1)−N(4)−C(3)	109.6(3)	C(5)−N(4)−C(3)	112.0(4)
Ni(1)−N(8)−C(7)	120.4(3)	Ni(1)−N(8)−C(9)	110.3(3)
C(7)−N(8)−C(9)	111.5(4)	Ni(1)−N(11)−C(10)	105.7(3)
Ni(1)−N(11)−C(12)	121.2(4)	C(10)−N(11)−C(12)	109.3(5)
N(1)−C(2)−C(3)	106.0(5)	N(4)−C(3)−C(2)	107.0(4)
N(4)−C(5)−C(6)	109.5(3)	N(4)−C(5)−C(15)	111.7(4)
C(6)−C(5)−C(15)	116.3(4)	C(5)−C(6)−C(6′)	111.7(3)
C(5)−C(6)−C(7)	115.2(3)	C(6′)−C(6)−C(7)	111.0(3)
N(8)−C(7)−C(16)	112.0(4)	N(8)−C(7)−C(6)	110.0(3)
C(16)−C(7)−C(6)	115.9(4)	N(8)−C(9)−C(10)	106.4(4)
N(11)−C(10)−C(9)	106.2(4)	N(11)−C(12)−C(13)	111.0(6)
C(14)−C(13)−C(12)	111.7(7)	N(1)−C(14)−C(13)	112.0(6)

so-called *trans III* conformation,[13] having two chair six-membered and two gauche five-membered chelate rings. Two Ni(II) ions are positioned as far apart as possible; the distance between the Ni(II) ions is 8.297 Å. Both central Ni(II) ions are square-planar low-spin four-coordinate; the average value of the Ni−N bonds is 1.937 Å, which is typical of square-planar tetraazamacrocyclic Ni(II) complexes.[14] The chirality due to a pair of asymmetric carbons in both macrocycles is C*-*meso* (5*R*)(*S*),7*S*(*R*)); we call this a *meso-meso* isomer. The most remarkable feature of the dimeric macrocycle is the configuration of the methyl groups on the fifth and seventh positions. In the *C*-meso* isomer of the corresponding monomacrocyclic Ni(II) complex, **2** (Figure 1b), the methyl groups occupy equatorial positions on the six-membered chelate rings,[12] whereas they occupy axial positions in the dimer. The positional relation of the two methyl groups in one macrocycle is 1,3-diaxial, which is unfavorable for a six-membered chelate ring, because of large steric repulsion between the methyl groups (the CH_3---CH_3 distance is 3.176 Å). We consider that such an unusual configuration is ascribable to one of bimacrocyclic effects, *i.e.*, the effect produced by closely connecting two macrocycles. When the linkage mode of the bridge is taken into account, assuming that both macrocycles in the *meso*−*meso* isomer adopt the "*trans III*" form, the following three configurational isomers are considered (Figure 2): (1) both bridge ends are equatorial (*eq*) with respect to the chair-form six-membered chelate ring and all methyl groups (Me) are axial (*ax*); (2) one bridge end is *eq* (Me: *ax*) and the other end is *ax* (Me: *eq*); (3) both bridge ends are *ax* (all Me: *eq*). The isomer 1 was indeed observed and isolated in this work. Preliminary MM2 calculations[15] supported that the first isomer (relative strain energy: 0 kJ mol^{-1}) is the most strain free, the second one (8.9 kJ mol^{-1}) is more strained than isomer 1, and the third one (40 kJ mol^{-1}) is the most strained. They suggest that much larger repulsion would be anticipated between the 1,3-equatorial methyl groups of one macrocycle and the other macrocyclic skeleton. The dimer complex should avoid such a repulsion to adopt the 1,3-diaxial methyl groups and the equatorial linkage of the two macrocyclic rings. Thus, the linkages of the macrocycles and the configuration of the methyl groups are strongly restricted in the bimacrocyclic structure.

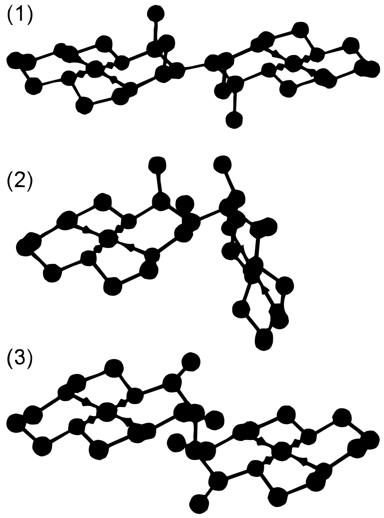

Figure 2. Proposed isomers of **1** due to *eq*−*eq* (1), *eq*−*ax* (2), and *ax*−*ax* (3) bridges.

Behavior in Aqueous Solution. The vis absorption spectrum of $\mathbf{1}(ClO_4)_4$ in water is quite different from that of corresponding monocyclic complex $\mathbf{2}(ClO_4)_2$ having C*-*meso* configuration (Figure S1, Supporting Information). The bimacrocyclic complex **1** shows a single absorption band at $\lambda_{max} = 444$ nm with $\epsilon_{max} = 157$ M^{-1} cm^{-1}, which can be ascribed to square-planar species, while **2** shows three bands in the visible region, λ_{max} (ϵ_{max}) = 337 nm (7.3), 460 (22), and 673 (2), due to the equilibrium between the square-planar (*ca*. 25%) and the water-coordinated octahedral species (*ca*. 75%).[12] The major reason for the dissimilarity is a difference in capability for accepting axially coordinating water molecules between **1** and **2**. Previous studies[16] have shown that axial methyl groups on the 5-, 7-, 12-, and 14-positions of a 14-membered tetraazamacrocyclic ring prevent the coordination of water molecules to the central Ni(II) ion; i.e., complexes having the axial methyl groups predominantly exist as square-planar species in aqueous solutions, while the ones with only equatorial methyl groups prefer water-coordinated octahedral species. In the present case, bimacrocyclic complex **1**, which has only axial methyl groups on the 5- and 7-positions as shown by X-ray crystallography, produces only the square-planar species. Accordingly, the proximate linkage of two macrocycles significantly changes the capability for accepting axially coordinating water molecules.

Catalytic Properties for Photochemical CO_2 Reduction. The catalytic activity of the thus obtained and characterized dinickel(II) complex was investigated for its photochemical reduction of CO_2 in an aqueous solution. We used the photochemical system consisting of the three components $[Ru^{II}(bpy)_3]^{2+}$ as the photosensitizer, ascorbic acid as the sacrificial

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(13) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

(14) Curtis, N. F. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum Press: New York, 1979; Chapter 4.

(15) A CAChe system (CAChe Scientific, Inc.) was used for MM2 calculations. Parameters were taken from those reported by Lindoy et al. (Adam, K. R.; Antolovich, M.; Brigden, L. G.; Lindoy, L. F. *J. Am. Chem. Soc.* **1991**, *113*, 3346). Conformation analysis of $[Ni(cyclam)]^{2+}$ was also performed as a check of our calculation. The results were essentially similar to those reported by Billo and Connolly (Connolly, P. J.; Billo, E. J. *Inorg. Chem.* **1987**, *26*, 3224) and Lindoy. Details will be reported elsewhere.

(16) Mochizuki, K.; Kondo, T. *Inorg. Chem.* **1995**, *34*, 6241 and literature cited therein.

Table 4. CO Generation in Photochemical CO_2 Reduction[a]

complex	amt of CO evolved[b]	rel ratio
1$(CF_3SO_3)_4$	1230	8.2
2$(ClO_4)_2$	180	1.2
2$(CF_3SO_3)_2$	195	1.3
3$(ClO_4)_4$	90	0.6
4(ClO_4)	ND[c]	
5$(ClO_4)_4$	ND[c]	
6$(ClO_4)_2$	150	1.0
6$(CF_3SO_3)_2$	165	1.1

[a] The aqueous sample solution contained 0.5 mmol dm^{-3} $[Ru^{II}(bpy)_3]Cl_2$, 0.5 mmol dm^{-3} Ni(II) ion (0.25 mmol dm^{-3} for dinickel(II) complexes), and 0.5 mol dm^{-3} ascorbic acid at pH 4. [b] Unit: μL. Experimental error ca. ±7%. [c] Not detected.

electron donor, and the Ni(II) complex as the catalyst, because the cyclam−Ni(II) complex, monomacrocyclic complex **6**, is well-known to act as a catalyst for the photochemical reduction of CO_2 in aqueous solutions[17] and analogous macrocyclic Ni(II) complexes have been extensively investigated.[18−20] Since CO_2 had been considered to be reduced to CO under the conditions of this photochemical system,[17−20] the amount of the evolved CO was measured by gas chromatography.[21] Although both the dimeric Ni(II) complex **1** and the corresponding monocyclic Ni(II) complex **2** also acted as the catalyst in the photochemical CO_2 reduction, these complexes were quite different in catalytic activity.[22] Table 4 summarizes the results of the CO generation along with the results of $[Ni^{II}(cyclam)](ClO_4)_2$, **6**$(ClO_4)_2$, and analogous Ni(II) complexes (for the time dependence of the CO generation using complex **1**; see Figure S2, Supporting Information). It was found that the bimacrocyclic dinickel(II) complex **1** acts as a better catalyst, generating CO more efficiently than the monomacrocyclic complexes. The bimacrocyclic complex **1**$(CF_3SO_3)_4$ produced 6.3−6.8 times the amount of CO compared with the corresponding monomacrocyclic Ni(II) complexes, **2**$(ClO_4)_2$ and **2**$(CF_3SO_3)_2$. In addition, **1** produced 7.5−8.2 times as much CO as $[Ni^{II}(cyclam)]^{2+}$ (**6**$(ClO_4)_2$ and **6**$(CF_3SO_3)_2$). On the other hand, the Ni(II) complex with bicyclam, **3**,[2] which has the same bimacrocyclic skeleton as **1** but without the methyl groups, generated only 60% of the amount of CO. The unreduced complexes having C═N double bonds, **4** and **5**, did not produce CO.

The simultaneous generation of H_2 under the same conditions as those described in Table 4 was also measured: **6**$(ClO_4)_2$, 350 μL; **1**$(CF_3SO_3)_4$, 83 μL. The generation ratio of CO/H_2 (v/v) is 15 for **1**$(CF_3SO_3)_4$, which is much larger than that of **6**$(ClO_4)_2$, 0.4; the CO/H_2 value, 0.11, was previously reported for **6**$(ClO_4)_2$ under conditions similar to ours.[17] The CO/H_2 ratio value for **1**$(CF_3SO_3)_4$ shows that the selectivity of **1** for the CO_2 reduction is markedly improved compared to that of the cyclam−Ni(II) complex.

From these results, we propose that both the dimeric structure with saturated macrocycles and the presence of axial methyl groups may play an important role in the appearance of such high activity and selectivity. One possible explanation is as follows: In the CO_2 reduction using macrocyclic metal complexes, CO_2-coordinated metal complex has been deduced to be an intermediate. A five-coordinate cobalt complex with the coordinated CO_2 was actually isolated,[23] which suggests a similar five-coordinated intermediate for the case of the present nickel complexes. Although complex **1** hardly forms six-coordinate species as described above, its structure seems to be suitable for the formation of the five-coordinate species. This peculiarity of the structure might be advantageous for the formation of the intermediate five-coordinated nickel complex with CO_2.

In conclusion, we emphasize that the bimacrocyclic Ni(II) complex, where two macrocycles are simply linked by a C−C bond, shows characteristic properties different from those of the corresponding monomacrocyclic Ni(II) complex.

Experimental Section

Synthesis of 1$(CF_3SO_3)_4$. (a) Preparation of 5$(ClO_4)_4$ by Dimerization of 4$(ClO_4)_2$. The starting compound **4**$(ClO_4)_2$ was prepared according to the reported method.[24] To an acetonitrile solution (300 mL) of **4**$(ClO_4)_2$ (20 g, 0.052 mol) was added an acetonitrile solution (150 mL) of $Fe(ClO_4)_3\cdot nH_2O$ (25 g; Wako Chemical) using a syringe. Before the addition, each solution had been bubbled by N_2 for 30 min. Yellow precipitates were immediately formed upon the addition. After the N_2 bubbling for a further 30 min, the yellow precipitate was filtered off, washed with cooled acetonitrile, and dried in vacuo (yield: 46%). *The perchlorate is potentially explosive*. For **5**$(ClO_4)_4$:[25] IR (KBr) 1660 cm^{-1} ($\nu_{C=N}$); FAB mass: *m/z* 861 $[M - ClO_4]^+$.

(b) Hydrogenation of 5$(ClO_4)_4$ and Isolation of the *meso−meso* Isomer of 1. To an $EtOH-H_2O$ (1:1 v/v) solution (300 mL) containing **5**$(ClO_4)_4$ (10 g) was added HCl until the solution reached pH 3. To the solution heated to 60 °C was added solid $NaBH_4$ (80 g) portionwise with stirring over a period of 1.5 h. During the addition of $NaBH_4$, the solution was kept at pH 3 by adding dilute HCl. As the reduction proceeded, black precipitates were formed. The solution was stirred at 60 °C for a further 30 min and adjusted to pH 1 with HCl to dissolve the black precipitates. The resulting clear orange solution was adjusted to pH 6 with NaOH, further stirred for 30 min, and evaporated to 50 mL. Ethanol was added to the solution to precipitate white solids composed mainly of NaCl, which were removed by filtration. The procedure for removal of the white solids, the reduction of the solution volume, addition of ethanol, and filtration was repeated three times. Then the solution was evaporated to dryness to yield an orange residue, which was dissolved in a minimum amount of water and put on the top of an SP-Sephadex C-25 column (l = 70 cm, ϕ = 3 cm). The adsorbed species were eluted with a mixed solution containing 0.05 M NaI and 0.3 M NaCl to give four well-separated bands. The first brown-orange band was identified as a monomacrocyclic Ni(II) complex composed mainly of **2**. Although the second and third bands were assumed to be other isomers due to the difference in the chirality of four asymmetric carbons, they have not yet been isolated. The fourth band was collected and isolated as perchlorate salts after removal of I^- and Cl^- (yield after three recrystallizations from water: 6%). Anal. Calcd for **1**$(ClO_4)_4\cdot 2H_2O$, $C_{24}H_{54}N_8Ni_2Cl_4O_{16}\cdot 2H_2O$: C, 28.66; H, 5.81;

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(17) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105.

(18) Tinnemans, A. H. A.; Koster, T. P. M.; Thewissen, D. H. M. W.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 288.

(19) Craig, C. A.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1990**, *94*, 7957.

(20) Kimura, E.; Wada, S.; Shionoya, M.; Takahashi, T.; Iitaka, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 397. Kimura, E.; Wada, S.; Shionoya, M.; Okazaki, Y. *Inorg. Chem.* **1994**, *33*, 770.

(21) Although generation of formic acid was investigated by an HPLC analysis (ODSII column, UV detector), we could not identify the peak due to formic acid because of the appearance of peaks proximate to that of formic acid. The peaks, probably due to the decomposition product of ascorbic acid, were observed in the photolysis even under a N_2 atmosphere.

(22) The electrochemical CO_2 reduction was also investigated by cyclic voltammetry (HMDE). Although the values of $E_{1/2}$ for $Ni^{II/I}$ are similar between **1** and **2** (**1**, −1.51 V *vs* Ag−AgCl; **2**, −1.49 V), peak currents, i_{pc}, of the catalytic wave for the CO_2 reduction are quite different (**1**, $E_{pc} = -1.35$ V, $i_{pc} = 20$ μA; **2**, $E_{pc} = -1.35$ V, $i_{pc} = 225$ μA). We speculate that the reason of this large difference in i_{pc} may be due to the difference between **1** and **2** in the adsorption of the complexes to the Hg electrode surface and in the CO_2-binding ability of the adsorbed complexes. The effects of axial methyl groups upon the electrochemical CO_2 reduction are described in a manuscript in preparation.[12]

(23) Fujita, E.; Szalda, D. J.; Creutz, D.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 4870.

(24) Martin, J. G.; Cummings, S. C. *Inorg. Chem.* **1973**, *12*, 1477.

(25) This complex is easily oxidized by air in solution to form the complex having five C═N bonds. Fab mass: *m/z* 859 $[M - ClO_4]^+$.

N, 11.14. Found: C, 28.63; H, 5.43; N, 11.05. FAB mass: *m*/*z* 869 $[M - ClO_4]^+$. Vis (H_2O): 444 nm (ϵ 157). Vis (CH_3NO_3): 457 nm (ϵ 159).

Free ligand was obtained by $CHCl_3$ extraction from an aqueous solution in which Ni(II) ions were removed from the complex prior to using the CN^- treatment. ^{13}C NMR ($CDCl_3$, TMS): δ 17.6 (CH_3), 28.7 (CH_2), 43.9 (CH), 47.6 (CH_2), 50.0 (CH_2), 51.5 (CH_2), 54.8 (CH). FAB mass: *m*/*z* 455 $[M + H]^+$.

1$(CF_3SO_3)_4$ was easily derived from the addition of $NaCF_3SO_3$ to an aqueous solution of the Cl^- form of **1**, which was prepared prior to passing the perchlorate through a Cl^--form anion-exchange resin. Yellow prismatic crystals of the triflate, which were used in X-ray crystallographic work, were obtained upon recrystallization from nitromethane. Anal. Found: C, 28.74; H, 4.63; N, 9.62. Calcd for **1**$(CF_3SO_3)_4$, $C_{28}H_{54}N_8Ni_2F_{12}S_4O_{12}$: C, 28.77; H, 4.66; N, 9.58. FAB mass: *m*/*z* 1017 $[M - CF_3SO_3]^+$. Vis (H_2O): 445 nm (ϵ 159). ^{13}C NMR (CD_3NO_2, TMS): δ 15.8 (CH_3), 27.3 (CH_2), 44.9 (CH), 49.1 (CH_2), 50.5 (CH_2), 52.5 (CH), 52.8 (CH_2).

6$(ClO_4)_4$,[26] **3**$(ClO_4)_4$,[2] and **2**$(ClO_4)_4$[12] were prepared according to the literature.

The triflates of mononuclear Ni(II) complexes were prepared by recrystallization of the corresponding chlorides from water in the presence of excess $NaCF_3SO_3$: for **6**$(CF_3SO_3)_2$, FAB mass *m*/*z* 405 $[M - CF_3SO_3]^+$; for **2**$(CF_3SO_3)_2$, FAB mass *m*/*z* 435 $[M - CF_3SO_3]^+$.

Physical Measurements. Visible absorption spectra were measured at 25 °C with a Hitachi 340 spectrophotometer. FAB mass spectra and ^{13}C NMR spectra were recorded on a JEOL JMS-DX303 spectrometer and JEOL JNM-FX90Q and JNM EX-270 spectrometers, respectively.

X-ray Crystallography. The determinations of the crystal class, orientation matrix, and accurate unit cell parameters were performed using a MAC Science MXC3k four-circle diffractometer (graphite-monochromatized Mo Kα radiation, $\lambda = 0.710\ 73$ Å). A yellow crystal (0.48 × 0.45 × 0.45 mm) was mounted. The intensity data were collected using the $\omega-2\theta$ scan technique in the region $3 < 2\theta < 55°$, but an absorption correction was not applied. A total of 6023 reflections were collected, of which 4198 independent significant reflections ($I \geq 3\sigma(I)$) were assumed to be observed. As a check of the crystal and electronic stability, three representative reflections were monitored at every 100 reflections; throughout the data collection, the intensities of these standards remained constant within experimental error. The structure was solved by direct methods (SIR 92) and refined using the full-matrix least-squares method. All the non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located by difference Fourier syntheses and included in the final refinement with the isotropic thermal parameters. The final refinement cycle included 406 variable parameters converged with $R = 0.059$ and $R_w = 0.054$ (weighing scheme: $w = \exp(10 \sin^2 \theta/\lambda^2)/\sigma^2(F_o)$). All the calculations were carried out on a Sun SPARK 10 work station (Crystan-GM program system provided by MAC Science).

Light Irradiation and Gas Analysis in Photochemical CO_2 Reduction. The sample solution (50 mL) containing 0.5 mmol dm^{-3} $[Ru^{II}(bpy)_3]Cl_2$, 0.5 mmol dm^{-3} Ni(II) ion (0.25 mmol dm^{-3} for the bimacrocyclic dinickel(II) complex or 0.5 mmol dm^{-3} for the mono-macrocyclic nickel(II) complex), and 0.5 mol dm^{-3} ascorbic acid at pH 4 was placed in a gastight flask (internal gas volume 163 mL). After CO_2 gas was passed through the solution for 30 min, it was irradiated by light (460 W ultra-high-pressure Hg lamp (Ushio UI-501C) with UV and IR light filters L-39 and RA-25S (Toshiba), water-filled round-bottom flask in front of the reaction cell) for 1 h at ca. 20 °C. Under these conditions, $[Ru(bpy)_3]^{2+}$ absorbs mainly in the 435 nm light band. After the irradiation, the gas products were immediately analyzed by gas chromatography (Shimadzu GC-14 gas chromatograph, TCD detector, molecular sieves 5A; carrier gas He for CO, Ar for H_2). The CO peak was identified by comparison of the retention time with that of the standard CO gas (GL Sciences). The quantity of CO was determined using the working curve which had been previously obtained using standard CO gas. The average value of at least three run times was used. The reproducibility of the data was checked three times along with changing examiners and lots of the Ni(II) complex. The deviation of each run from the average value was ca. ±7%. When any one of the three components was omitted, or N_2 was bubbled instead of CO_2, no CO was detected.

Supporting Information Available: Tables S1−S3, listing crystallographic data collection and processing parameters, hydrogen atom coordinates, and anisotropic thermal parameters for non-hydrogen atoms, and Figures S1 and S2, showing vis absorption spectra and time dependence of the CO generation (5 pages). Ordering information is given on any current masthead page.

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(26) Bosnich, B.; Tobe, M. L.; Webb, G. A. *Inorg. Chem.* **1965**, *4*, 1109.