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Crystal Structures of Mono- and Di-nuclear Nickel(II) Complexes Derived from the Substitution Reaction of [Ni(Me$_2$[14]dienatoN$_4$)]I and Each of Benzoyl Chloride and Isophthaloyl Dichloride

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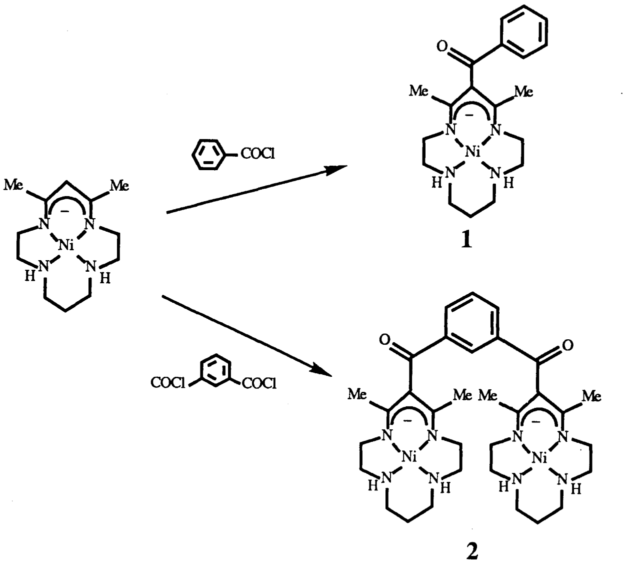
The reactions of (5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6-dienato)nickel(II) iodide with benzoyl chloride and isophthaloyl dichloride gave mononuclear **1** and dinuclear **2** nickel(II) complexes, respectively. Complex **1** crystallized in space group $P2_1/a$ with Z=4, a=23.704(10), b=7.726(3), c=11.581(4) Å, β=104.16(3)°, V=2056.5(1.4) Å^3. The benzoyl group is positioned at the 6 position of the macrocycle and tilted to the NiN$_4$ plane by 67.9° due to the steric hindrance from two methyl groups. Complex **2** crystallized in space group $P\bar{1}$ with Z=2, a=12.124(3), b=16.484(4), c=10.243(4) Å, α=94.84(3), β=111.04(3), γ=80.69(2)°, V=1884.6(1.1) Å^3. The metal ions are 12.777(6) Å apart, and the two coordination planes are nearly co-planar, the dihedral angle between them being 164.4°.

The charge-delocalized six-membered chelate rings exhibit quasi-aromatic properties.[1] The central carbon atom of the six-membered chelate ring has a pronounced nucleophilic character; this reactivity has been empolyed to introduce a variety of substituents into the chelate ring of the macrocycle. Busch *et al.* have introduced peripheral functional groups, or bridging groups, to (2,12-dimethyl-1,5,9,13-tetraazacyclohexadecan-1,3,9,11-tetraenato)nickel(II) [Ni(Me$_2$[16]tetraenatoN$_4$)], exhibiting two nucleophilic centers per complex and synthesized macrocyclic ligands having superstructure components or binucleating ligands having a face-to-face orientation, which may be useful models for biological molecules.[2,3] In previous paper[4] we have employed the substitution reaction of (5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6-dienato)nickel(II) salt [Ni(Me$_2$[14]dienatoN$_4$)]$^+$, exhibiting a nucleophilic center per complex with each benzoyl chloride and isophthaloyl dichloride; we obtained the substituted mononuclear **1** and dinuclear **2** nickel(II) complexes according to the reaction scheme shown below. In this study complexes **1** and **2** were subjected to a single-crystal X-ray diffraction study in order to confirm completion of the substitution reaction and to examine whether or not two metal ions of **2** are positioned in close proximity by the ligand framework.



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Experimental

Syntheses. A parent nickel(II) complex, (5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6-dienato)nickel(II) iodide, [Ni(Me$_2$[14]dienatoN$_4$)]I was prepared by the method of Cummings.[5] A substituted mononuclear complex (6-benzoyl-5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6-dienato)nickel(II) iodide [Ni(Me$_2$Benzyl[14]dienatoN$_4$)]I **1** and a dinuclear complex, [6,6′-isophthaloylbis[5,7-dimethyl-1,4,8,11-tetraazacylotetradeca-4,6-dienato]nickel(II)] iodide μ-iso[Ni(Me$_2$[14]dienatoN$_4$)]$_2$I$_2$·H$_2$O **2**, were prepared according to a method reported earlier.[4] Recrystallization from a methanol–water mixed solution gave large red prisms of **1**. Single-crystals of **2** suitable for a X-ray diffraction study were obtained as red plates by a diffusion method, in which a dichloromethane–methanol solution of the complex and a methanol–water were used. The crystals of **2** are quite soft and thin-plates. Attempts to carry out crystallization by the use of other anions, instead of iodide, have been unsuccessful to give viscous materials.

Crystallographic Study. The reflection data for both complexes were measured on a Rigaku Denki AFC-5 automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation at room temperature. The unit cell parameters and orientation matrixes were determined by means of least-squares analyses on 25 reflections (20°<2θ<30°). The standard reflections were monitored every 100 reflections, showing no systematic variations in the intensities. The reflection data were corrected for both Lorentz and polarization effects. Absorption corrections were made by using Furnas's empirical method,[6] based on ψ scans (ψ = 0—360°) of suitable reflections. The basic crystallographic parameters are listed in Table 1.

The structures were solved by the standard heavy-atom method and refined by the block-diagonal least-squares method, where the minimized function is $\sum w(|F_o|-|F_c|)^2$.

Table 1. Crystallographic Parameters for Data Collection and Structure Refinement

	1	**2**
Formula	$INiON_4C_{19}H_{27}$	$I_2Ni_2O_3N_8C_{32}H_{50}$
Fw	513.1	916.0
Space group	$P2_1/a$	$P\bar{1}$
a/Å	23.704(10)	12.124(3)
b/Å	7.726(3)	16.484(4)
c/Å	11.581(4)	10.243(4)
α/°	90.0	94.84(3)
β/°	104.16(3)	111.04(3)
γ/°	90.0	80.69(2)
V/Å^3	2056.5	1884.6
Z	4	2
D_{calcd}/g cm^{-3}	1.657	1.702
Cryst dimens/mm	0.2×0.3×0.3	0.06×0.2×0.2
μ(Mo $K\alpha$)/cm^{-1}	24.4	26.6
Transm factor	1.159—1.458	1.016—1.213
Scan-type	ω-2θ	ω-2θ
Scan width/°	1.2+0.35tan θ	1.2+0.35tan θ
Scan speed/° min^{-1}	2	2
Observed reflection with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	3122	3374
Final R	0.0727	0.0979
Final R_w	0.0523	0.1030

$R=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$ and $R_w=[\Sigma w[+F_o|-|F_c|)^2/\Sigma w+F_o|^2]^{1/2}$

Table 2. Positional Parameters (×10^{-4}) of **1** for Non-Hydrogen Atoms

Atom	x	y	z	$B_{\mathrm{eq}}$$^{a)}$
I	1490(0)	4974(1)	3177(1)	5.2
Ni	860(0)	934(1)	3814(1)	3.1
O	483(3)	2266(8)	8264(6)	5.7
N1	292(3)	1964(8)	4446(6)	3.0
N2	305(3)	982(9)	2281(6)	3.5
N3	1429(3)	−356(8)	3175(6)	3.7
N4	1363(3)	685(8)	5279(6)	3.1
C1	−255(3)	2267(11)	3513(8)	4.0
C2	−106(4)	2393(11)	2350(8)	4.1
C3	506(4)	1252(12)	1182(8)	4.6
C4	930(4)	−142(13)	1031(8)	4.9
C5	1500(4)	23(13)	1986(7)	4.4
C6	1983(3)	−207(12)	4073(8)	4.2
C7	1873(3)	−427(11)	5245(8)	4.2
C8	1318(3)	1244(10)	6318(7)	3.2
C9	1790(4)	805(12)	7434(8)	4.6
C10	817(4)	2122(10)	6484(7)	3.4
C11	316(3)	2340(10)	5539(7)	3.1
C12	−231(3)	3137(10)	5822(8)	3.9
C13	822(4)	2761(11)	7671(8)	4.1
C14	1265(3)	4145(11)	8231(7)	3.6
C15	1586(3)	5006(11)	7526(8)	4.0
C16	1999(4)	6208(12)	8084(9)	5.2
C17	2083(4)	6550(13)	9258(9)	5.8
C18	1771(4)	5748(12)	9935(8)	5.7
C19	1357(4)	4534(10)	9411(8)	4.2

a) B values for anisotropic refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $(4/3)[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab\cos\gamma B_{12}+ac\cos\beta B_{13}+bc\cos\alpha B_{23}]$.

In the least-squares calculations, since the weights (such as $1/\sigma(|F_o|)^2$ and $1/\sigma(|F_o|)$) did not give more satisfactory results than did the equal weight, the equal weight ($w=1$) was adopted. The hydrogen atoms bound to the carbon atoms were positioned at the calculated positions and were included in the structure factor calculations, but not refined. The disagreement factor of **2** was somewhat large, probably due to the large temperature factors of iodine atoms. The atomic-scattering factors were taken from the literature.[7)] All computations were performed on a FACOM M 780 computer at the Computer Center of Kyushu University using the UNICS III program system.[8)] The final atomic coordinates of the non-hydrogen atoms for **1** and **2** are given in Tables 2 and 3, respectively. Tables of observed and calculated structure factors, listing of atomic positional and anisotropic thermal parameters of non-hydrogen atoms, atomic parameters of hydrogen atoms, complete lists of bond distances and angles with their estimated standard deviations have been deposited as Document No. 8976 at the Office of the Editor of Bull.Chem. Soc. Jpn.

Results and Discussion

ORTEP drawings of **1** and **2** with the atom numbering schemes are shown in Fig. 1 and 2, respectively. An

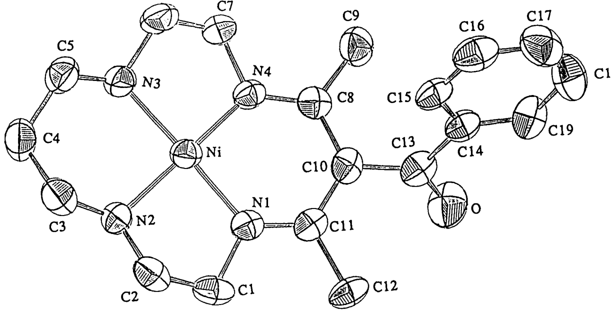


Fig. 1. ORTEP view (50% probability level) of **1** with the atom numbering scheme.

Table 3. Positional Parameters ($\times 10^{-4}$) of **2** for Non-Hydrogen Atoms

Atom	x	y	z	B_{eq}[a)]	Atom	x	y	z	B_{eq}[a)]
I1	13624(2)	6974(2)	7236(2)	12.0	C11	11536(14)	3290(10)	8908(18)	3.0
I2	2316(2)	10218(1)	1218(3)	12.8	C12	11645(19)	3770(11)	10284(20)	4.8
Ni1	12070(2)	1789(2)	7578(3)	4.2	C13	10211(16)	4490(10)	7698(21)	4.0
Ni2	3260(2)	7303(1)	1891(2)	2.6	C14	8886(15)	4804(9)	7022(16)	2.8
O1	10861(12)	4984(8)	8261(20)	7.5	C15	8052(16)	4312(11)	6977(18)	3.5
O2	7748(11)	7266(8)	6002(15)	5.3	C16	6818(17)	4657(13)	6386(20)	4.6
N1	12224(12)	2589(8)	8929(14)	3.4	C17	6535(16)	5439(12)	5940(19)	4.1
N2	13522(15)	1195(10)	8773(22)	6.7	C18	7382(15)	5927(11)	6002(17)	3.3
N3	11882(17)	854(12)	6335(23)	7.4	C19	8555(14)	5592(10)	6579(16)	2.9
N4	10748(12)	2392(9)	6307(15)	3.8	C20	7052(15)	6765(11)	5441(20)	3.7
N5	4581(12)	6536(8)	2082(13)	2.7	C21	5450(17)	8176(12)	5833(17)	4.1
N6	2572(13)	6826(9)	−3(14)	4.0	C22	5059(15)	7632(10)	4524(16)	2.8
N7	1906(12)	8149(8)	1685(14)	3.5	C23	5895(14)	6982(9)	4314(15)	2.5
N8	3964(12)	7791(8)	3630(13)	2.8	C24	5646(16)	6476(9)	3107(18)	3.0
C1	13127(20)	2293(13)	10272(20)	5.1	C25	6678(17)	5878(11)	2896(20)	3.9
C2	14111(23)	1754(16)	9942(28)	8.0	C26	4476(17)	5959(11)	842(20)	4.1
C3	14310(27)	883(25)	8081(39)	14.3	C27	3158(19)	5951(13)	125(20)	5.0
C4	13973(29)	454(21)	6776(35)	10.8	C28	1273(19)	6874(13)	−681(20)	4.8
C5	12816(27)	687(16)	5737(30)	8.3	C29	633(18)	7738(14)	−694(23)	5.5
C6	10653(21)	1048(13)	5200(25)	6.3	C30	680(16)	8015(13)	758(23)	4.9
C7	10327(19)	1906(12)	4926(18)	4.8	C31	1913(17)	8365(12)	3072(21)	4.5
C8	9557(18)	3572(13)	5036(17)	4.3	C32	3174(18)	8501(12)	3999(19)	4.5
C9	10340(14)	3159(11)	6384(17)	3.1	OW	12277(32)	−982(25)	7391(36)	21.5
C10	10670(14)	3618(10)	7664(16)	2.4					

a) B values for anisotropic refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $(4/3)[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab\cos\gamma B_{12}+ac\cos\beta B_{13}+bc\cos\alpha B_{23}]$.

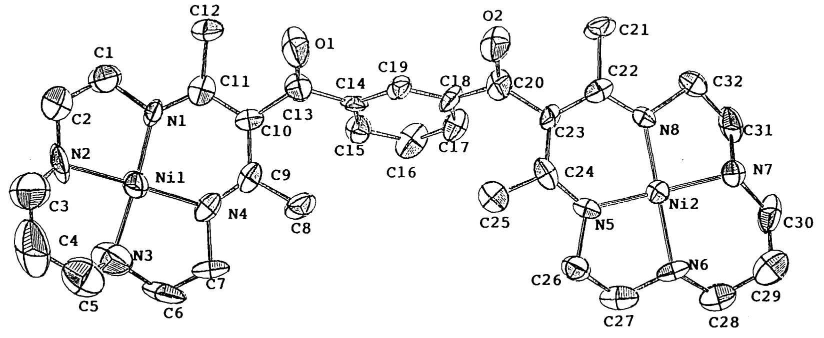


Fig. 2. ORTEP view (50% probability level) of **2** with the atom numbering scheme.

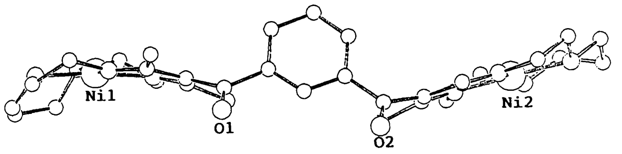


Fig. 3. Edge-on view of **2** showing relative orientation of two Ni coordination spheres.

Table 4. Selected Bond Distances and Angles of **1**

(a) Bond distances (Å)				
	Ni-N1	1.861(6)	Ni-N2	1.932(7)
	Ni-N3	1.959(7)	Ni-N4	1.826(6)
(b) Bond angles (deg)				
	N1-Ni-N2	87.6(3)	N2-Ni-N3	92.2(3)
	N3-Ni-N4	86.8(3)	N1-Ni-N4	92.8(3)

edge-on view of **2** is shown in Fig. 3. The relevant interatomic bond distances and angles of **1** and **2** are given in Tables 4 and 5, respectively.

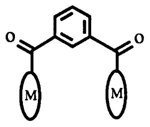
An X-ray analysis of **1** confirmed the completion of the substitution reaction at the central carbon atom of the diiminate six-membered chelate ring of the macrocycle. The benzoyl group is substituted at the 6 position of the macrocycle, and tilted to the coordination plane NiN_4 by 67.9°, due to a steric hindrance from the two methyl groups at 5 and 7 positions. The nickel(II) ion is coordinated with two iminate and two secondary amine nitrogen atoms to form a square planar coordination geometry. The four Ni–N bond distances fall into two groups, attributed to a difference between the iminate

Table 5. Relevant Bond Distances and Angles of **2**

(a) Bond distances (Å)			
(a-1) Coordination sphere around Ni1			
Ni1-N1	1.81(2)	Ni1-N2	1.91(2)
Ni1-N3	1.90(2)	Ni1-N4	1.86(2)
(a-2) Bridging moiety			
C10-C13	1.46(3)	O1-C13	1.19(3)
C13-C14	1.52(3)	C14-C15	1.38(3)
C14-C19	1.36(2)	C15-C16	1.44(3)
C16-C17	1.35(3)	C17-C18	1.38(3)
C18-C19	1.37(2)	O2-C20	1.23(3)
(a-3) Coordination sphere around Ni2			
Ni2-N5	1.83(2)	Ni2-N6	1.97(2)
Ni2-N7	1.93(2)	Ni2-N8	1.85(2)
(b) Bond angles(deg)			
(b-1) Coordination sphere around Ni1			
N1-Ni1-N2	88.4(8)	N2-Ni1-N3	88(1)
N3-Ni1-N4	90.8(9)	N1-Ni1-N4	93.3(7)
(b-2) Bridging moiety			
O1-C13-C14	118(2)	C13-C14-C15	120(2)
C13-C14-C19	119(2)	C15-C14-C19	122(2)
C14-C15-C16	117(2)	C15-C16-C17	119(2)
C16-C17-C18	123(2)	C17-C18-C19	117(2)
C14-C19-C18	122(2)	C17-C18-C20	122(2)
C19-C18-C20	121(2)	C18-C20-O2	117(2)
C18-C20-C23	120(2)	O2-C20-C23	123(2)
(b-3) Coordination sphere around Ni2			
N5-Ni2-N6	86.4(7)	N6-Ni2-N7	94.4(7)
N7-Ni2-N8	86.1(6)	N5-Ni2-N8	93.0(6)

and secondary amine nitrogen atoms. The Ni–N(iminate) bond distances of 1.826(6)—1.861(6) Å are shorter than the Ni–N(amine) distances of 1.932(7)—1.959(7) Å . The saturated six-membered chelate-ring takes a chair-conformation and two five-membered chelate rings take a gauche conformation. The structural feature is quite similar to that of the parent complex, [Ni(Me$_2$[14]dienatoN$_4$)]$^+$.[4)]

An X-ray analysis of **2** confirmed a dinuclear structure of the complex obtained from the reaction of [Ni(Me$_2$[14]dienatoN$_4$)]$^+$ and isophthaloyl dichloride in the 2 : 1 mole ratio. Three conformations (**a**, **b**, and **c**) are considered for **2** with respect to the mutual orientation of the two {NiN$_4$} chromophores. Among them, isomer **a** has a co-facial structure which can be expected to have cooperative effect of the two metal ions, and can serve as a useful model for biological molecules. As can clearly be seen in Fig. 3, complex **2** crystallized under the condition undertaken in this study corresponds to conformer **b**. The metal ions are 12.777(6) Å apart and the two coordination planes are nearly co-planar; the dihedral angle between two coordination planes being 164.4°. The isophthaloyl group is tilted to two coordination planes by 118.7° (Ni1) and 110.01° (Ni2). The coordination geometries around the two nickel(II) ions are both square planar, being consistent with the fact that the complex is diamagnetic. The Ni–N bond distances fall into two groups, attributed to the difference between iminate (1.81(2)—1.86(2) Å) and secondary amine (1.90(2)—1.91(2) Å) nitrogen atoms. The saturated six-membered chelate-rings take a chair-conformation, and the five-membered chelate rings take a gauche conformation.



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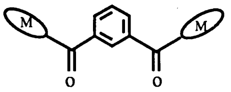

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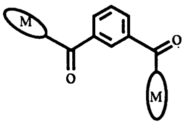

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