The Crystal Structure of a Nickel(III) Complex with *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane, [Ni^{III}Cl$_2$(Me$_6$[14]aneN$_4$)]ClO$_4$

MASAHIRO YAMASHITA*

College of General Education, Nagoya University, Furocho, Chikusa-ku, Nagoya 464, Japan

and HIROSHI MIYAMAE

Department of Chemistry, Faculty of Science, Josai University, Keyakidai, Sakado-shi, Saitama 350-02, Japan

Abstract

The crystal structure of a nickel(III) complex with *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (= Me$_6$[14]aneN$_4$), [Ni^{III}Cl$_2$(Me$_6$[14]aneN$_4$)]ClO$_4$, has been determined by single crystal X-ray diffraction method. The complex crystallizes in the monoclinic space group $A2/a$ with $a = 15.634(1)$, $b = 6.5378(6)$, $c = 21.707(2)$ Å, $\beta = 92.29(1)°$ and $Z = 4$. The nickel atom is surrounded octahedrally by four nitrogens and two chloro atoms in the *trans* form. The macrocyclic ligand adopts the most stable conformation and the total stereochemistry is the same as that of the corresponding Ni(II) analog, *trans*-[Ni^{II}Cl$_2$(Me$_6$[14]ane-N$_4$)]. The coordination bond lengths of this compound are significantly shorter than those in the Ni(II) analog, but a little longer than those of [Ni^{III}-Cl$_2$([14]aneN$_4$)]ClO$_4$ which has no methyls in the macrocyclic ligand. These results are consistent with those of the ESR and electronic spectra previously reported.

Introduction

The chemistry of nickel(III) has recently received much attention from various viewpoints such as an unusual oxidation state [1], a trace bio-element [2], and kinetics and mechanisms of the oxidation of organic molecules or metals [3]. So far a number of nickel(III) complexes have been prepared. However, even if the compounds appear to be 'nickel(III) complexes' based on the empirical formula, they could belong to the following groups; (a) discrete intrinsic nickel(III) complexes (e.g. [NiCl$_2$([14]-aneN$_4$)]ClO$_4$) [4], (b) nickel(II) complexes with cation radical ligands (e.g. [NiCl$_2$(diars)$_2$]Cl) [5], (c) halogen-bridged one-dimensional nickel(II)–nickel(IV) mixed-valence complexes (e.g. Ni(en)$_2$-Cl(ClO$_4$)$_2$) [6], and (d) partially oxidized com-

plexes (e.g. Ni(Hdpg)$_2$I) [7]. Among these 'nickel-(III) complexes', most of those with tetraazacyclo-tetradecanes belong to group (a) and are well-characterized by physicochemical methods. They are low-spin d^7 *trans*-[NiX$_2$N$_4$]$^+$ types with one unpaired electron in the d$_{z^2}$ orbital [8]. Busch noted that the ease of oxidation to Ni(III) decreases as the size of the hole in the center of the macro-cycle increases successively in the ligands, [14]-aneN$_4$, [15]aneN$_4$, and [16]aneN$_4$ except for [13]-aneN$_4$ [9]. Busch *et al.* also investigated the effect of axial anions (X) to the electronic structures of Ni(III) in [NiX$_2$(Me$_2$[14]aneN$_4$)]ClO$_4$ by ESR and electronic spectra, and showed the observed λ values (spin–orbit coupling constants obtained by the correlation, $g_\perp = 2 - 6\lambda/\Delta$) follow the nephelauxetic series [10].

Although so far there are a number of electro-chemical, absorption spectral, ESR, and magnetical investigations, only a few crystal structures have been reported [4, 11, 12]. Moreover, there is little discussion on the correlation between crystal structures and electronic states. In this study, we determined the crystal structure of [Ni^{III}Cl$_2$(Me$_6$[14]-aneN$_4$)]ClO$_4$ and compared it with those of the corresponding [Ni^{II}Cl$_2$(Me$_6$[14]aneN$_4$)] [13] and [Ni^{III}Cl$_2$([14]aneN$_4$)]ClO$_4$ which has no methyls in the macrocyclic ligand [4] (Fig. 1). We also discussed the correlation between the structures and electronic states based on the results of ESR and electronic spectra of [NiCl$_2$(Me$_6$[14]aneN$_4$)]ClO$_4$ and [NiCl$_2$([14]aneN$_4$)]ClO$_4$ previously reported [14].
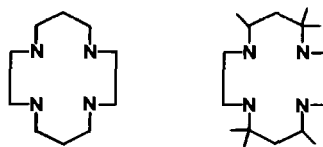

Fig. 1. Macrocyclic ligands and their abbreviations: left, 1,4,8,11-tetraazacyclotetradecane (= [14]aneN$_4$); right, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (= Me$_6$[14]aneN$_4$).

---

*Author to whom correspondence should be addressed.

Experimental

Synthesis

The compound was prepared by the method previously described [15]. The single crystals suitable for X-ray work were obtained by recrystallization from acetonitrile solution.

Crystal Data

Formula $C_{16}H_{36}N_4O_4Cl_3Ni$, molecular weight = 509.5, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), monoclinic, space group $A2/a$, $a = 15.634(1)$, $b = 6.5378(6)$, $c = 21.707(2)$ Å, $\beta = 92.29(1)°$, $V = 2218.2(4)$ Å^3, $D_x = 1.525$, $D_m = 1.556$ g cm^{-3}, $Z = 4$, $F(000) = 1068$, μ(Mo $K\alpha$) = 1.27 mm^{-1}. Crystal dimensions were *ca.* $0.1 \times 0.1 \times 0.7$ mm.

Data Collection and Processing

3339 reflections in the range of $2\theta \leqslant 60°$ ($h \geqslant 0$, $k \geqslant 0$ and $l \gtrless 0$) were collected by the $2\theta-\theta$ scan mode on a Rigaku AFC-5 four circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation. During data collections three standard reflections, monitored every 100 measurements, exhibited no significant decay in the intensities. The unit cell dimension was refined from a least-squares fit of 29 unique 2θ values ($26° < 2\theta < 33°$).

2624 independent reflections with $|F| \geqslant 3\sigma(|F|)$ were used for structural determination. Intensities were corrected for Lorentz and polarization factors, but not for absorption and extinction.

Structure Analysis and Refinement

The structure was solved by the heavy-atom method to locate the NiCl$_2$ skeleton. Successive Fourier maps gave the coordinates of the remaining non-H atoms. The parameters were refined by the block-diagonal least-squares method using the UNICS III program system [16], minimizing $\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w|F_o|^2$ with $w = 1/(\sigma(F)^2 + 0.02 \times |F_o|^2)$. The H atoms were located from a difference Fourier map and refined assuming isotropic thermal parameters. Complex neutral atom scattering factors were referred from a standard table [17]. The final conventional R converged at 0.042 and R_w at 0.041 with $S = 1.4177$.

The final atomic parameters with estimated standard deviations are listed in Table 1.

Results and Discussion

The perspective drawing of the compound with the numbering system is presented in Fig. 2. Relevant bond lengths and angles are listed in Table 2. The Ni^{III} ion is required to be at the center of symmetry and surrounded pseudo-octahedrally by four secondary nitrogens of the macrocyclic ligand and two

TABLE 1. Atomic Parameters[a]

Atom	x	y	z	B_{eq}
Ni	50000	25000	25000	1.35(1)
Cl(2)	25000	−36358(18)	0	3.48(3)
Cl(1)	59033(4)	55867(9)	24275(3)	2.17(2)
N(1)	55845(12)	22249(30)	33379(8)	1.65(5)
N(2)	40729(12)	42643(29)	27994(9)	1.60(5)
C(1)	51525(15)	23882(41)	39488(10)	2.00(6)
C(5)	61806(16)	4725(41)	32981(11)	2.21(6)
C(4)	66094(15)	6492(41)	26953(11)	2.13(6)
C(3)	37509(16)	38422(38)	34266(11)	2.04(6)
C(2)	44805(17)	40822(40)	39014(11)	2.34(7)
C(31)	30086(19)	52724(50)	35802(13)	3.16(8)
C(11)	58289(19)	30614(49)	44385(13)	3.11(8)
C(12)	47704(18)	3429(45)	41294(12)	2.70(7)
O(1)	17693(21)	−24632(52)	−1668(16)	8.38(12)
O(2)	27067(17)	−48699(54)	−5089(12)	6.65(10)
H(N1)	590(2)	332(4)	332(1)	2.7(6)
H(N2)	432(2)	550(4)	282(1)	3.0(6)
H(C21)	478(2)	533(4)	382(1)	2.0(5)
H(C22)	424(2)	416(4)	430(1)	2.9(6)
H(C31)	355(1)	256(4)	341(1)	1.6(5)
H(C51)	661(2)	54(4)	364(1)	2.8(6)
H(C52)	587(2)	−77(4)	330(1)	2.6(6)
H(111)	606(2)	434(5)	432(1)	4.1(7)
H(112)	628(2)	220(4)	449(1)	3.2(7)
H(113)	555(2)	323(5)	481(1)	4.4(8)
H(121)	523(2)	−64(4)	424(1)	2.9(6)
H(122)	445(2)	−17(5)	382(1)	3.0(6)
H(123)	447(2)	56(5)	448(1)	3.5(7)
H(311)	322(2)	671(5)	354(1)	3.8(7)
H(312)	253(2)	504(5)	330(1)	3.9(7)
H(313)	285(2)	503(5)	398(1)	3.9(7)
H(C41)	697(1)	−52(4)	264(1)	1.6(5)
H(C42)	695(2)	179(4)	267(1)	2.9(6)

[a]Positional parameters are multiplied by 10^5 ($\times 10^3$ for H atoms). Thermal parameters are given by the equivalent temperature factors (Å^2).

chloro atoms in the *trans* form. The macrocyclic ligand adopts the most stable conformation; the two six-membered rings take the chair form with the C(3)–CH$_3$ bonds in equatorial positions; the five-membered rings are in the gauche conformation. The N–Ni–N angle contained in the five-membered ring is less than 90° while that in the six-membered ring is more than 90°.

The Ni–Cl(1) bond inclines almost towards the N(1) atom to avoid the steric hindrance of the axial methyl group on the six-membered ring, being the Cl(1)–Ni–N(1) bond angle of 83.69(6)°. The degree of the inclination of the Ni–Cl bond in this compound is larger than that in [Ni^{III}Cl$_2$([14]aneN$_4$)]-ClO$_4$. Thus the electrostatic repulsion between the Ni–Cl(1) and Ni–N(1) bonds causes the Ni–N(1) bond to be longer than the Ni–N(2) bond.
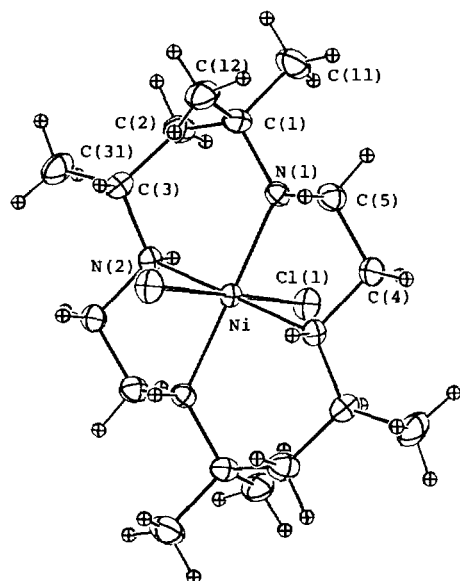
Fig. 2. Structure of [NiCl₂(Me₆[14]aneN₄)]⁺ cation with atom numbering drawing by ORTEP [18]. Thermal ellipsoids are at 50% probability level except for the H atoms.

To neutralize the net charge in the unit cell, the ClO_4^- anion is on a crystallographic two-fold axis. [Ni^{III}Cl₂(Me₆[14]aneN₄)]ClO₄ is packed in a distorted zinc blende structure in which two of the cation—anion distances are short and the other two are long. The NiN₄ plane makes an angle of *ca.*

54.3° with respect to the *b* axis, and the Ni—Cl(1) bond *ca.* 35.2°. In this connection, the NiN₄ planes are parallel between those arranged in the *ac* plane, but they are almost perpendicular between those arranged along the *b* axis (Fig. 3).

The total stereochemistry is the same as that of the corresponding Ni(II) analog, *trans*-[Ni^{II}Cl₂-(Me₆[14]aneN₄)]. However, the coordination bond lengths of *trans*-[Ni^{III}Cl₂(Me₆[14]aneN₄)]⁺ (Ni–N = 1.983(2) and 2.011(2) Å; Ni–Cl = 2.4721(6) Å) are significantly shorter than those in the Ni(II) analog (Ni–N = 2.060(3) and 2.102(3) Å; Ni–Cl = 2.562(1) Å). The bond lengths and angles within the organic ligand in the Ni(III) complex are normal. The Ni^{III}–N bond lengths in this compound are almost equal to those in [Ni^{III}(H₂PO₄)₂(Me₆[14]-aneN₄)]ClO₄ which has the same in-plane macrocyclic ligand (Table 3) [11].

On the other hand, compared with [NiCl₂([14]-aneN₄)]ClO₄ which has no methyls in the in-plane macrocyclic ligand, the Ni–N and Ni–Cl bond lengths in [NiCl₂(Me₆[14]aneN₄)]ClO₄ are meaningfully a little longer. The total stereochemistries in both compounds are the same as each other except for the methyls in the in-plane macrocyclic ligand. Such difference in the coordination bond lengths around the Ni(III) between these compounds is assumed to affect the electronic states.

The results of the ESR and electronic spectra of these compounds previously obtained are listed

TABLE 2. Bond Distance (A) and Angles (°)

[NiCl₂(Me₆[14]aneN₄)]⁺ cation					
Ni–Cl(1)	2.4721(6)	Ni–N(1)	2.011(2)	Ni–N(2)	1.983(2)
N(1)–C(1)	1.416(3)	N(1)–C(5)	1.482(3)	N(2)–C(3)	1.496(3)
N(2)–C(4ⁱ)	1.484(3)	C(1)–C(2)	1.528(4)	C(1)–C(11)	1.534(4)
C(1)–C(12)	1.522(4)	C(2)–C(3)	1.515(4)	C(3)–C(31)	1.538(4)
C(4)–C(5)	1.498(4)				
Cl(1)–Ni–N(1)	83.69(6)	Cl(1)–Ni–N(2)	88.48(6)		
Cl(1)–Ni–N(1ⁱ)	96.31(6)	Cl(1)–Ni–N(2ⁱ)	91.52(6)		
N(1)–Ni–N(2)	93.88(8)	N(1)–Ni–N(2ⁱ)	86.12(8)		
Ni–N(1)–C(1)	125.6(1)	Ni–N(1)–C(5)	106.6(3)		
Ni–N(2)–C(3)	117.9(1)	Ni–N(2)–C(4ⁱ)	107.4(1)		
C(1)–N(1)–C(5)	114.2(2)	C(3)–N(2)–C(4ⁱ)	114.0(2)		
N(1)–C(1)–C(2)	108.8(2)	N(1)–C(1)–C(11)	107.9(2)		
N(1)–C(1)–C(12)	110.9(2)	C(2)–C(1)–C(11)	107.0(2)		
C(2)–C(1)–C(12)	112.2(2)	C(11)–C(1)–C(12)	109.9(2)		
C(1)–C(2)–C(3)	117.9(2)	N(2)–C(3)–C(2)	109.2(2)		
N(2)–C(3)–C(31)	111.7(2)	C(2)–C(3)–C(31)	110.2(2)		
N(1)–C(5)–C(4)	107.2(2)	N(2ⁱ)–C(4)–C(5)	107.5(2)		
ClO₄⁻ anion					
Cl(2)–O(1)	1.412(3)	Cl(2)–O(2)	1.416(3)		
O(1)–Cl(2)–O(2)	108.5(2)	O(1)–Cl(2)–O(1ⁱⁱ)	114.2(2)		
O(1)–Cl(2)–O(2ⁱⁱ)	107.6(2)	O(2)–Cl(2)–O(2ⁱⁱ)	110.5(2)		

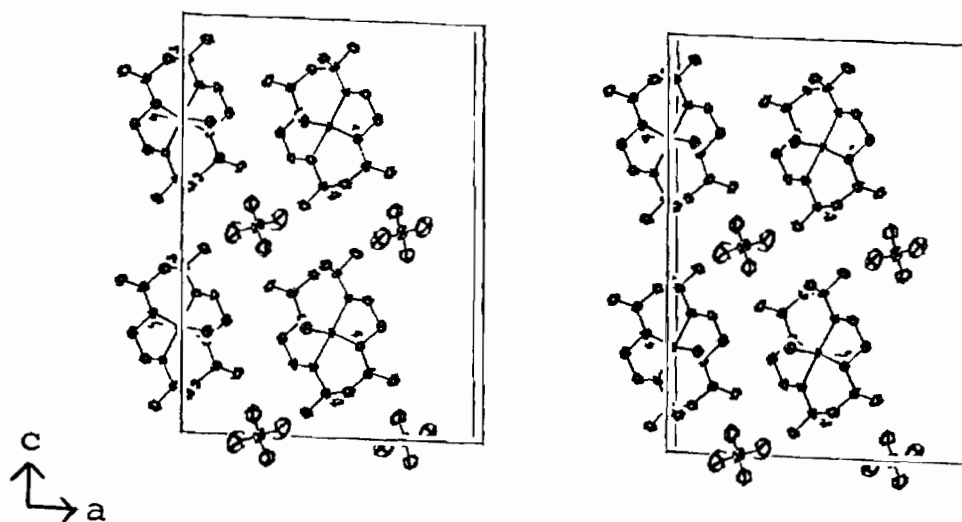Symmetry operations: ^{i} $-x, \frac{1}{2}-y, \frac{1}{2}-z$; ^{ii} $\frac{1}{2}-x, y, -z$.

Fig. 3. Stereoscopic packing diagram of the unit cell contents.

TABLE 3. Comparison of Relevant Bond Distances (A) of Ni(II) and Ni(III) Complexes with N_4-macrocyclic Ligands

	[Ni^{II}Cl$_2$(Me$_6$- [14]aneN$_4$)]	[Ni^{III}Cl$_2$(Me$_6$- [14]aneN$_4$)]ClO$_4$	[Ni^{III}(H$_2$PO$_4$)$_2$- (Me$_6$[14]aneN$_4$)]ClO$_4$	[Ni^{III}Cl$_2$([14]- aneN$_4$)]ClO$_4$	[Ni^{III}(NCS)$_2$- ([14]aneN$_4$)]ClO$_4$
Ni–Cl	2.562(1)	2.4721(6)		2.456(1) 2.447(1)	
Ni–N	2.060(3) 2.102(3)	1.983(2) 2.011(3)	1.992(3) 1.994(3) 2.007(3) 2.019(3)	1.963(4) 1.965(4) 1.973(4) 1.979(3)	1.965(2) 1.979(2)
Reference	13	this work	11	4	12

TABLE 4. Results of ESR and Electronic Spectra [14]

	g_0	$g_\perp$	$g_\parallel$	$A_\parallel$ (G)	d–d ($\times 10^3$ cm^{-1})	
[NiCl$_2$([14]aneN$_4$)]ClO$_4$	2.133	2.184	2.022	26.0	10.70	13.33
[NiCl$_2$(Me$_6$[14]aneN$_4$)]ClO$_4$	2.142	2.201	2.028	25.3	10.26	12.66

in Table 4 [14]. The ESR spectra showed axial patterns with the parallel features split into seven almost spaced lines of relative intensity *ca.* 1:2:3:4: 3:2:1, indicating that the Ni(III) ions are hexa-coordinated with four nitrogen atoms of the macro-cycles in the single-plane and two Cl atoms in the axial positions. This implies that the structures around the Ni(III) ions in the solutions are the same as those in the solids. The $A_\parallel$ value of [NiCl$_2$-(Me$_6$[14]aneN$_4$)]ClO$_4$ (25.3 G) is smaller than that of [NiCl$_2$([14]aneN$_4$)]ClO$_4$ (26.0 G), indicating that the covalent bond between Ni and Cl atoms in the former is weaker than that in the latter. This is

in agreement with the results of the crystal struc-tures.

In the electronic spectra, they show two d–d bands. Busch *et al.* assigned the higher energy band to the transition of $d_{xz}, d_{yz} \rightarrow d_{z^2}$. Such a transition in [NiCl$_2$(Me$_6$[14]aneN$_4$)]ClO$_4$ is lower than that in [NiCl$_2$([14]aneN$_4$)]ClO$_4$. The spin–orbit coupling constant λ in the former (-424.1 cm^{-1}) is smaller than that in the latter (-408.8 cm^{-1}), indicating that the covalency around the Ni(III) ion in the former is weaker than that in the latter.

Such results of the ESR and electronic spectra are consistent with those of the crystal structures.

Supplementary Material

Anisotropic thermal parameters and structure factors are available from the corresponding author on request.

References

1 D. H. Busch, C. G. Pillsbury, F. V. Lovecchio, A. M. Tait, Y. Hung, S. Jackels, M. C. Rakowski, W. P. Schammel and Y. L. Martin, *A.C.S. Symposium, Ser., 38* (1977) 32; K. Nag and A. Chakravorty, *Coord. Chem. Rev., 33* (1979) 87; R. J. Haines and A. McAuley, *Coord. Chem. Rev., 39* (1981) 77; D. W. Margerum, *Pure Appl. Chem., 77* (1983) 23.

2 S. J. P. Albracht and E. C. Graf, *FEBS Lett., 140* (1982) 311; J. R. Lancaster, *Science, 216* (1982) 1324; A. J. Thomson, *Nature (London), 298* (1982) 602.

3 J. C. Brodovitch, A. McAuley and T. Oswald, *Inorg. Chem., 21* (1982) 3442; E. Kimura, A. Sakonaka, R. Machida and M. Kodama, *J. Am. Chem. Soc., 104* (1982) 4255; C. F. Wells and D. Fox, *J. Chem. Soc., Dalton Trans.,* (1977) 1502.

4 T. Ito, M. Sugimoto, K. Toriumi and H. Ito, *Chem. Lett.,* (1981) 1477.

5 P. Kreisman, R. Marsh, J. R. Preer and H. B. Gray, *J. Am. Chem. Soc., 90* (1968) 1067.

6 M. Yamashita, Y. Nonaka, S. Kida, Y. Hamaue and R. Aoki, *Inorg. Chim. Acta, 52* (1981) 43; M. Yamashita, I. Murase, 1. Ikemoto and T. Ito, *Chem. Lett.,* (1985) 1133; M. Yamashita and T. Ito, *Inorg. Chim. Acta, 87* (1984) L5.

7 M. Cowie, A. Gleizes, G. W. Grynkewich, D. W. Kalina, M. S. McIwre, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby, J. A. Ibres, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc., 101* (1979) 2922.

8 A. Desideri, J. B. Raynor and C.-K. Poon, *J. Chem. Soc., Dalton Trans.,* (1977) 2051.

9 D. H. Busch, *Acc. Chem. Res., 11* (1978) 392.

10 E. S. Gore and D. H. Busch, *Inorg. Chem., 12* (1973) 1.

11 E. Zeigerson, I. Bar, J. Bernstein, L. J. Kirschenbaum and D. Meyerstein, *Inorg. Chem., 21* (1982) 73.

12 M. Yamashita, K. Toriumi and T. Ito, *Acta Crystallogr., Sect. C, 41* (1985) 1607.

13 T. Ito and K. Toriumi, *Acta Crystallogr., Sect. B, 37* (1981) 88.

14 M. Yamashita, *Dr. Thesis,* Kyushu University, 1982.

15 N. F. Curtis and D. F. Cook, *Chem. Commun.,* (1967) 962.

16 T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku, 55* (1979) 69.

17 J. A. Ibers and W. C. Hamilton (eds.), *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, 1974, p. 74.

18 C. K. Johnson, *ORTEP II, Report ORNL-5138,* revised, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.