Synthesis and Structure of (Nitroacetato)((7*RS*,14*RS*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II), [Ni(na)(Me_6[14]aneN_4)]

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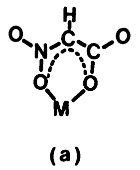
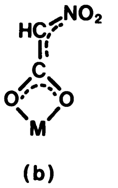
Synopsis. The title compound, [Ni(na)(Ma_6[14]aneN$_4$)], has been synthesized by the reaction of α-[Ni(Me_6[14]aneN$_4$)](ClO_4)$_2$ with potassium nitroacetate (K_2na) in water. X-Ray analysis shows that the complex is a *cis*-NiO_2N_4 type with the tetraazamacrocycle folded, and that a dianionic nitroacetate (na^{2-}) chelates the nickel(II) with one oxygen atom of the CO_2^- moiety and one oxygen atom of the NO_2^- moiety to form a six membered chelate ring.

Much attention has been paid to the formation of a new C–C bond using CO_2 as carbon source.[1,2] α-Nitro acids, for example, were obtained by the treatment of primary nitroparaffins with CO_2 in the presence of Mg(OCH_3)$_2$[3] or $MgCl_2$ and triethylamine.[4] The driving force of the reaction was attributed to the formation of a stable magnesium(II) chelate of α-nitro carboxylate ion during the reaction, since the free anion of α-nitro carboxylate is susceptible to decarboxylation. However, no direct structural evidence has been reported.

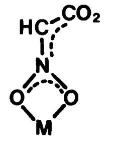
Aiming at the deeper understanding of the CO_2 uptake chemistry of this type, we intended in this study to prepare and isolate nitroacetato complex and to know its chemical properties. Another point of interest is the structure of the coordinated nitroacetate ion. There are three possible structures for the nitroacetato chelate, as shown below.



(a)



(b)



(c)

The type (a) is a six-membered chelate like the acetylacetonate. The type (b) and (c) are of four-membered chelate similar to that formed by carboxylate or nitroalkanoate ion, respectively.

The complex, [Ni(na)(Me_6[14]aneN_4)], was prepared from α-[Ni(Me_6[14]aneN_4)](ClO_4)$_2$[5] and K_2na. The complex shows three d-d bands typical of octahedral nickel(II), at 10,200 (ε=23), 17,400 (ε=13), and *ca.* 27000 (shoulder) cm^{-1}. Figure 1 shows an ORTEP view of the complex and the atom numbering system. The complex adopts *cis*-NiO_2N_4 structure with the tetraazamacrocycle folded, and the na chelate ring was found to take the type (a) structure. The atomic coordinates of non-hydrogen atoms and relevant bond distances and angles are given in Tables 1 and 2, respectively.

The N(A)O(1)O(3)C(B) and the C(A)O(2)O(4)C(B) moieties are planar within experimental errors. These two planes are not coplanar but are tilted each other by 17.3(3)°. The C(A)–C(B) distance (1.421(9)) Å is longer than C–C distances found in acetylacetonate chelates.[6] These facts indicate that the π-electrons are not fully delocalized over the six-membered ring.

The assignments of the N(A) and C(A) atoms are not unique, but they are tentatively assigned to the nitrogen (NO_2^-) and the carbon (CO_2^-) atoms, respectively, on the basis of the examination of the reliability factors and the thermal parameters.[7] No statistical disorder between NO_2^- and CO_2^- was

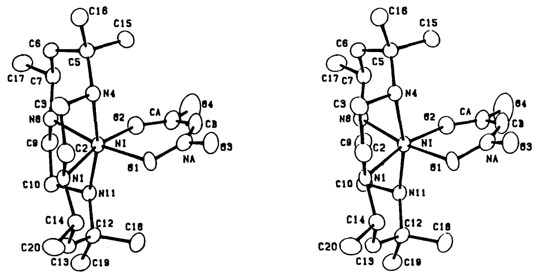


Fig. 1 ORTEP view of [Ni(na)(Me_6[14]aneN_4)] along with the atom numbering scheme.

TABLE 1. FRACTIONAL COORDINATES ($\times 10^5$) FOR NON-HYDROGEN ATOMS

Atom	*x*	*y*	*z*
Ni	21960(3)	3365(4)	11401(6)
O(1)	23870(18)	16340(23)	21753(37)
O(2)	14581(18)	10080(26)	-3284(37)
O(3)	20078(23)	28358(27)	33761(51)
O(4)	7711(35)	21507(41)	-11835(77)
N(1)	31019(20)	-1149(26)	24975(39)
N(4)	17098(21)	-34(29)	31178(42)
N(8)	18444(21)	-9694(28)	2094(40)
N(11)	27789(21)	3819(27)	-7827(41)
N(A)	19293(24)	22615(31)	22177(53)
C(A)	12153(30)	18161(41)	-1774(74)
C(B)	13896(33)	23772(39)	11431(83)
C(2)	29244(27)	-1283(40)	40659(51)
C(3)	22275(28)	-5494(40)	40877(54)
C(5)	10029(26)	-4345(35)	29712(55)
C(6)	9800(27)	-13116(36)	19590(60)
C(7)	11154(28)	-12194(37)	3128(59)
C(9)	20134(30)	-9397(40)	-13879(54)
C(10)	27237(28)	-5824(37)	-14041(52)
C(12)	34870(27)	7794(36)	-6205(52)
C(13)	39344(26)	3363(36)	7356(55)
C(14)	37273(25)	4393(36)	23322(53)
C(15)	5009(28)	3048(40)	22781(64)
C(16)	7966(31)	-7038(41)	45421(61)
C(17)	8859(35)	-21115(48)	-5517(75)
C(18)	34166(32)	18349(39)	-4097(62)
C(19)	38369(31)	6116(46)	-20614(60)
C(20)	43390(28)	1864(46)	35072(61)
O(W)	21064(31)	15192(40)	-40327(59)
O(M)	7908(36)	17755(52)	-38451(81)
C(M)	5184(46)	27424(63)	-46587(113)

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observed. The uncoordinated oxygen atom, O(3), is involved in intermolecular hydrogen bonds,⁸⁾ while the uncoordinated oxygen atom O(4) is not. There seems to be a difference in the ability of the hydrogen bond formation between the oxygen atoms of the CO_2^- and NO_2^- moieties.

The nitroacetato ligand in this complex is fairly stable toward decarboxylation, especially in methanol. The stability is attributed to the formation of the stable six-membered nitroacetato chelate, as has been postulated for the magnesium(II) complex, and to the macrocyclic effect of the ligand $Me_6[14]aneN_4$ that can fold.⁹⁾

Experimental

Materials. α-$[Ni(Me_6[14]aneN_4)](ClO_4)_2$⁵⁾ and K_2na¹⁰⁾ were prepared according to the literatures.

$[Ni(na)(Me_6[14]aneN_4)]\cdot CH_3OH\cdot H_2O$. To an aqueous suspension (10 cm³) of α-$[Ni(Me_6[14]aneN_4)](ClO_4)_2$ (1.08 g, 2 mmole), K_2na (0.45 g, 2.5 mmole) dissolved in a small amount of water was added. The yellow solids disappeared quickly, and blue violet solids were formed. These were filtered and extracted with methanol to remove $KClO_4$. Vacuum evaporation at 30 °C gave blue violet crystals (0.78 g). These were recrystallized from methanol. The elemental analysis was consistent with the above chemical formula. IR (KBr disk, between 1150 and 1600 cm⁻¹): 1580, 1550, 1453, 1392, 1295, and 1170 cm⁻¹.

X-Ray Analysis. A single crystal of $[Ni(na)(Me_6[14]aneN_4)]\cdot CH_3OH\cdot H_2O$ with approximate dimension 0.56×0.42×0.38 mm was used for the X-ray study. Diffraction data were obtained on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo $K\alpha$ radiation. Intensities were corrected for Lorentz and polarization factors. Crystal data are: monoclinic, $P2_1/n$, $a=19.710(4)$, $b=14.274(2)$, $c=8.833(1)$ Å, $\beta=97.13(2)°$, $V=2466.1(7)$ Å³, $Z=4$, $D_x=1.34$ g cm⁻³, $\mu(\text{Mo } K\alpha)=0.83\text{mm}^{-1}$. The structure was solved by the heavy atom method and refined by block-diagonal least-squares method. The weighting scheme, $w=[\sigma_{\text{count}}^2+(0.015|F_o|)^2]^{-1}$, was employed. All the hydrogen atoms except that of hydroxyl group of methanol were located by the difference Fourier syntheses and included in the final refinement with the isotropic temperature factors. The final R indices were $R=0.062$ and $R_w=0.075$ for 3344 independent reflections ($2\theta<50°$) with $|F_o|>3\sigma(|F_o|)$.¹¹⁾ Calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System, UNICS III.¹²⁾

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References

1) R. Eisenberg and D. E. Hendriksen, *Adv. Catal.*, **28** 79 (1979).

2) "Organic and Bioorganic Chemistry of Carbon Dioxide," ed by S. Inoue, N. Yamazaki, Kodansha, Tokyo (1981).

3) M. Stiles and H. L. Fiukbeiner, *J. Am. Chem. Soc.*, *81*, 505 (1959).

4) N. Matsumura, Y. Yagyu, and E. Imoto, *Nippon Kagaku Kaishi*, **1976**, 1801.

5) L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4092 (1969); The symbols, α, β, and γ, denote (1*RS*, 4*RS*, 8*RS*, 11*RS*)-, (1*RS*, 4*SR*, 8*RS*, 11*SR*)-, and (1*RS*, 4*RS*, 8*SR*, 11*SR*)-form. The β- and γ-isomers did not react nicely with K_2na, since they can hardly fold to form octahedral complexes.

6) For example, T. Ito, K. Toriumi, F. B. Ueno, and K. Saito, *Acta Crystallogr., Sect B*, **36**, 2998 (1980).

7) If N(A) and C(A) are assinged to carbon and nitrogen, respectively, the reliability factors raised to $R=0.064$ and $R_w=0.078$. At the same time, the thermal parameters (B_{eq}) of N(A) and C(A) became too small and too large, respectively, as compared with those of other atoms within the chelate ring.

8) O(3)···O(W)*=2.948(8) Å where O(W) is water of crystallization; O(3)···N(1)*=3.027(6), and O(3)···N(8)*=2.968(7) Å. Key to symmetry operation: (x, y, $1+z$) for O(W)*, and ($1/2-x$, $1/2+y$, $1/2-z$) for N(1)* and N(8)*.

9) H. Ito and T. Ito, *Bull. Chem. Soc. Jpn.*, **58**, 1755 (1985).

10) W. Steinkopf, *Ber.*, **42**, 3925 (1909).

11) Tables of hydrogen atom coordinates, anisotropic thermal parameters, and observed and calculated structure factors are kept in the office of the Chemical Society of Japan (Document No. 8529).

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

TABLE 2. RELEVANT BOND DISTANCES (l/Å) AND ANGLES (ϕ/°) WITH THEIR e.s.d.'s (IN PARENTHESES)

Ni	-O(1)	2.079(3)	O(1)	-N(A)	1.275(6)
Ni	-O(2)	2.061(3)	O(3)	-N(A)	1.305(6)
Ni	-N(1)	2.124(4)	O(2)	-C(A)	1.262(7)
Ni	-N(4)	2.150(4)	O(4)	-C(A)	1.262(9)
Ni	-N(8)	2.119(4)	N(A)	-C(B)	1.345(8)
Ni	-N(11)	2.167(4)	C(A)	-C(B)	1.422(9)

O(1)	-Ni	-O(2)	86.4(1)	N(4)	-Ni	-N(8)	87.7(2)
O(1)	-Ni	-N(1)	85.9(1)	N(4)	-Ni	-N(11)	167.7(2)
O(1)	-Ni	-N(4)	85.3(2)	N(8)	-Ni	-N(11)	84.4(2)
O(1)	-Ni	-N(8)	170.8(2)	Ni	-O(1)	-N(A)	123.3(3)
O(1)	-Ni	-N(11)	103.5(1)	Ni	-O(2)	-C(A)	127.3(4)
O(2)	-Ni	-N(1)	167.1(2)	O(1)	-N(3)	-O(3)	116.7(4)
O(2)	-Ni	-N(4)	105.4(2)	O(1)	-N(5)	-C(B)	124.5(5)
O(2)	-Ni	-N(8)	89.6(1)	O(3)	-N(5)	-C(B)	118.9(5)
O(2)	-Ni	-N(11)	83.9(1)	O(2)	-C(A)	-O(4)	120.7(6)
N(1)	-Ni	-N(4)	84.3(2)	O(2)	-C(A)	-C(B)	123.1(5)
N(1)	-Ni	-N(8)	99.4(2)	O(4)	-C(A)	-C(B)	116.1(6)
N(1)	-Ni	-N(11)	87.8(2)	N(A)	-C(B)	-C(A)	126.8(6)