

## Reaction Product of N-Salicylaldehyde-N'-acetylacetonethylenediamino-copper(II) with *p*-Nitrobenzenediazonium, Accompanying a Rearrangement of the Coordination Sphere

NAOHIDE MATSUMOTO\*, TOMOKO ISHIDA, CHIKAKO YOSHIMURA and AKIRA OHYOSHI

Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860, Japan

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### Abstract

The asymmetrical quadridentate copper(II) complex N-salicylaldehyde-N'-acetylacetonethylenediaminocopper(II) and the analogous complexes react with *p*-nitrobenzenediazonium tetrafluoroborate to produce the substituted *p*-nitrophenylazo complex which is coordinated by an oxygen, two imine and an azo nitrogens through a rearrangement of coordination sphere from N<sub>2</sub>O<sub>2</sub> chromophore of the parent complexes. The reaction products were characterized by elemental analyses, infrared, <sup>1</sup>H NMR and electronic spectra, and by single-crystal X-ray analysis.

### Introduction

Goddard [1] investigated the reaction of bis-(acetylacetonethylenediaminometal(II) and phenyldiazonium salts and found that the substituted phenylazo derivatives are coordinated by two imine and two azo nitrogens, *i.e.*, the substitution reaction accompanies a rearrangement of coordination sphere from the N<sub>2</sub>O<sub>2</sub> chromophore to the N<sub>4</sub> chromophore of the reaction products, as shown in Fig. 1.

In this study, the substitution reaction of *p*-nitrobenzenediazonium tetrafluoroborate and the copper(II) or nickel(II) complexes with asymmetrical quadridentate Schiff bases derived from 1:1:1 condensation products of salicylaldehyde (or *o*-hydroxyacetophenone), ethylenediamine and acetylacetonethylenediamine have been employed, in order to study whether the rearrangement reaction shown in Fig. 1 can occur or not. The reaction products were characterized by elemental analyses, infrared, <sup>1</sup>H NMR and electronic spectra. The reaction product, N-*o*-hydroxyacetophenone-N'-acetylacetonethylenediaminonickel(II) and *p*-nitrobenzenediazonium tetra-

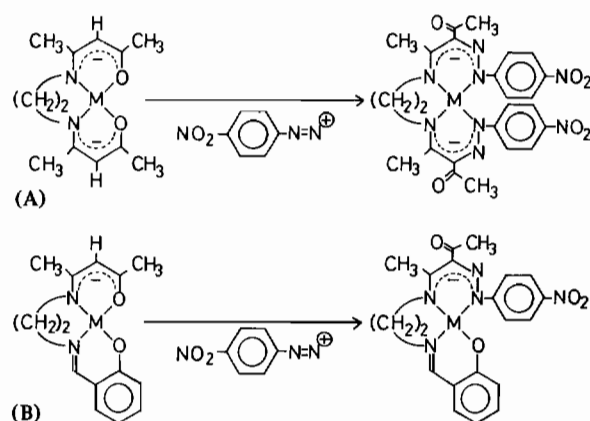


Fig. 1. (A) Reaction scheme from M(acacen-H) and *p*-nitrobenzenediazonium to M(acacen-E); (B) Reaction scheme from [ML1-H] and *p*-nitrobenzenediazonium to [ML1-E].

fluoroborate, was also subjected to a single-crystal X-ray analysis.

### Experimental

#### Physical Measurements

Elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. Thermal analyses (TG, DTA) were performed on a Rigaku Denki thermal analyzer, Model 8113 RH, under argon atmosphere. Visible and ultraviolet spectra were obtained with a Hitachi recording spectrophotometer 323, and infrared spectra were recorded as KBr disks with a JASCO A-702 spectrophotometer. The 100 MHz <sup>1</sup>H NMR spectra were recorded on a JEOL MH 100 spectrometer, using CDCl<sub>3</sub> as the solvent and SiMe<sub>4</sub> as the internal reference at room temperature.

#### Synthesis

##### Parent Copper(II) complexes

The asymmetrical quadridentate Schiff base copper(II) complexes, N-salicylaldehyde-N'-acetylacetonethylenediaminocopper(II) and N-*o*-hydroxyacetophenone-N'-acetylacetonethylenediaminocopper(II) were synthesized by the reaction of the Schiff base ligand with copper(II) acetate dihydrate in the presence of ethylenediamine.

\*Author to whom correspondence should be addressed.

ethylenediaminocopper(II) and N-*o*-hydroxyacetophenone-N'-acetylacetonethylenediaminocopper(II) were prepared by the methods described earlier [2–4] and identified by the elemental analyses, where the complexes are abbreviated as [CuL1–H] and [CuL2–H], respectively.

#### Ligands

The ligands [H<sub>2</sub>L1–H] and [H<sub>2</sub>L2–H] were obtained by demetallation reaction of the corresponding copper(II) complexes with gaseous hydrogen sulfide in dichloromethane, according to the procedures described earlier [3, 4].

#### Parent Nickel(II) Complexes

The nickel(II) complexes [NiL1–H] and [NiL2–H] were prepared by mixing nickel(II) acetate tetrahydrate and the corresponding ligands in methanol, according to the method described earlier [3].

#### Reaction Products of Parent Copper(II) or Nickel(II) Complexes with *p*-Nitrobenzenediazonium Tetrafluoroborate

The reaction procedures of parent copper(II) or nickel(II) complexes with *p*-nitrobenzenediazonium tetrafluoroborate are essentially similar and the reaction procedure of [CuL1–H] with *p*-nitrobenzenediazonium tetrafluoroborate is exemplified in detail. The solution of [CuL1–H] (3.2 g, 10 mmol) was cooled at 0 °C and solid *p*-nitrobenzenediazonium tetrafluoroborate (2.4 g, 10 mmol) was slowly added with vigorous stirring. After half an hour, trimethylamine (1.0 g, 10 mmol) was added and stand for several hours in a refrigerator. The resulting precipitates were collected, washed with a small amount of dichloromethane and diethyl ether, and dried *in vacuo*. The products were recrystallized from a mixture of dichloromethane and *n*-hexane.

#### X-Ray Diffraction

Brown needle crystals of [NiL2–E] as hemidichloromethane suitable for X-ray diffraction study were prepared by a diffusion method at room temperature, where the solvents used were dichloromethane and *n*-hexane. A crystal with approximate dimensions of 0.2 × 0.3 × 0.5 mm was used. Unit-cell parameters and intensity data were obtained on a Rigaku Denki AFC-5 automated four-circle diffractometer with a monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.710730$  Å). Unit-cell parameters were determined on 25 reflections in the range of  $20^\circ < 2\theta < 30^\circ$ . Crystal data: C<sub>21</sub>H<sub>21</sub>N<sub>5</sub>O<sub>4</sub>Ni·0.5CH<sub>2</sub>Cl<sub>2</sub>, F.W. = 508.6, triclinic, space group =  $P\bar{1}$ ,  $a = 12.334(3)$ ,  $b = 14.164(5)$ ,  $c = 7.717(2)$  Å,  $\alpha = 112.23(3)$ ,  $\beta = 96.21(3)$ ,  $\gamma = 111.12(2)^\circ$ ,  $V = 1116.4(8)$  Å<sup>3</sup>,  $D_x = 1.513$  ( $Z = 2$ ),  $D_m = 1.522$  g cm<sup>-3</sup>

(by the flotation method in aqueous KI solution),  $\mu(\text{Mo K}\alpha) = 10.2$  cm<sup>-1</sup>.

Intensity data were collected by the  $\theta$ – $2\theta$  scan technique with a scan rate of 4° min in  $2\theta$ . For weak reflections the peak scan was repeated up to three times, depending on their intensities. Three standard reflections were monitored every 100 reflections throughout the set to confirm no occurrence of decay in intensity. A total of 3514 reflections with  $2.5^\circ < 2\theta < 50^\circ$  were collected, of which independent 3462 reflections with  $|F_o| > 3\sigma(|F_o|)$  were considered as observed reflections and used for structural analysis. Intensity data were corrected for the Lorentz and polarization effects but not for absorption.

#### Solution and Refinement of the Structure

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. In the least-squares procedure, the function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1$ . The neutral atomic scattering factors for H, C, O, Ni and Cl were taken from International Tables for X-ray Crystallography, Vol. IV [5]. Anomalous dispersion corrections for all the component atoms were also taken from the literature. All calculations were carried out on a FACOM M-200 computer at the Computer Center of Kyushu University by the use of a local version of the UNICS III [6, 7]. The position of the nickel atom was determined from a three-dimensional Patterson synthesis, and all the non-hydrogen atoms (except for the crystal solvent) were located from subsequent Fourier and difference Fourier syntheses. The dichloromethane molecule as crystal solvent was subjected to disorder. The occupancy factors were assigned to the atoms located in the difference Fourier synthesis according to the peak heights. Hydrogen atoms were determined from the difference Fourier synthesis. The final least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen and disordered atoms gave  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 7.08$ , and  $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 7.49\%$ . The final difference Fourier synthesis showed no significant features except for several diffuse peaks around the crystal solvent region (*ca.* 1.2 eÅ<sup>-3</sup>). Final positional parameters with their estimated standard deviations are given in Table I. Lists of structure factors, anisotropic thermal parameters, and positional parameters for hydrogen atoms are available.

#### Results and Discussion

Elemental analytical data are given in Table II, along with the selected infrared frequencies assignable to the C=O stretching mode. As indicated

TABLE I. Atomic Parameters of [NiL2-E], where the Positional Parameters are multiplied by 10<sup>4</sup>, and the Thermal Parameters are given by the Equivalent Temperature Factors.

Atom	x	y	z	B <sub>eqv</sub>
Ni	1565(1)	3589(1)	1145(1)	2.57(2)
O1	2277(4)	5013(4)	3152(7)	3.71(16)
O2	2095(6)	-92(5)	378(10)	6.43(26)
O3	7378(6)	8397(5)	3999(10)	6.50(25)
O4	8371(5)	7580(5)	4783(10)	6.92(27)
N1	31(5)	3578(4)	718(8)	2.83(18)
N2	837(5)	2071(4)	-653(7)	2.92(18)
N3	3101(5)	3578(4)	1331(7)	2.60(17)
N4	3297(5)	2709(4)	1229(8)	3.06(19)
N5	7442(6)	7582(5)	4102(9)	4.65(23)
C1	1796(6)	5701(5)	3839(9)	3.15(23)
C2	2594(7)	6805(6)	5363(11)	4.36(28)
C3	2186(8)	7562(6)	6287(11)	4.96(32)
C4	970(9)	7306(7)	5756(12)	4.92(34)
C5	183(7)	6260(6)	4241(12)	4.34(31)
C6	564(6)	5447(5)	3238(10)	3.04(24)
C7	-297(6)	4348(6)	1620(10)	3.07(24)
C8	-1598(7)	4143(7)	999(13)	4.69(33)
C9	-903(6)	2462(6)	-877(11)	3.79(25)
C10	-294(6)	1813(6)	-2003(10)	3.74(24)
C11	1218(6)	1323(5)	-773(9)	3.26(23)
C12	511(7)	99(6)	-2277(11)	4.63(28)
C13	2417(6)	1664(5)	418(9)	3.08(23)
C14	2812(7)	855(6)	686(12)	4.50(29)
C15	4133(9)	1241(9)	1550(19)	8.04(53)
C16	4212(5)	4574(5)	2025(9)	2.55(20)
C17	4215(6)	5462(5)	1638(10)	3.14(23)
C18	5271(6)	6449(5)	2326(10)	3.45(24)
C19	6314(6)	6525(5)	3350(10)	3.30(22)
C20	6353(6)	5648(6)	3691(9)	3.29(23)
C21	5292(6)	4665(5)	3016(9)	2.92(22)

by elemental analysis, the complexes [CuL2-E] and [NiL2-E] were crystallized as solvates. The crystal solvents were detected by thermogravimetric analysis, where the weights losses attributable to the crystal solvents were observed. In addition to the thermal analysis, <sup>1</sup>H NMR spectra for [NiL2-E] also detected the crystal solvent. Infrared spectra of the reaction products of the parent complexes with *p*-nitrobenzenediazonium tetrafluoroborate differ from those

of the corresponding parent complexes, most notably in the appearance of an intense band at *ca.* 1650 cm<sup>-1</sup>, as given in Table II. Goddard [1] studied the reaction of bis(N-acetylacetonate)ethylenediaminocopper(II) and phenyldiazonium tetrafluoroborate and elucidated that the substituted phenylazo derivative is coordinated by two imine and two azo nitrogens through a coordination rearrangement from the N<sub>2</sub>O<sub>2</sub> chromophore of the parent Cu(ac<sub>2</sub>en), based on the appearance of an intense band at *ca.* 1650 cm<sup>-1</sup> in the infrared spectra which is assignable to C=O stretching of the free acetyl group. Based on the analogy of a reaction of M(ac<sub>2</sub>en) with phenyldiazonium salt, the present reaction product has a structure as shown in Fig. 1, where the product consists of a N<sub>3</sub>O coordination chromophore through a coordination rearrangement.

The <sup>1</sup>H NMR spectra were measured to verify the substitution on the  $\gamma$ -position of the acetylacetonato residue. The methine proton resonance of the acetylacetonate residue of the parent nickel(II) complex (4.9 ppm) disappeared in those of the substituted complexes, supporting the introduction of the substituent at this position.

The electronic spectra of the reaction products, along with those of the parent complexes, are shown in Fig. 2. As shown in Fig. 2, the substituted complexes exhibit an absorption at *ca.* 22 × 10<sup>3</sup> cm<sup>-1</sup> for the copper complex and at *ca.* 20 × 10<sup>3</sup> cm<sup>-1</sup> for the nickel complex with an extinction coefficient of 6600–15000 mol<sup>-1</sup> cm<sup>2</sup>. The band is attributable to the phenyldiazonium chromophore.

#### Molecular Structure of [NiL2-E]

The molecular structure together with the atom labelling system used is shown in Fig. 3. Relevant bond distances and angles are listed in Table III\*.

A significant feature of the structure is the unique identification of the rearrangement of the coordination sphere, in which the nickel ion is square planar

\*Tables of: (i) atomic parameters of hydrogen atoms and crystal solvent and (ii) mean square displacement tensor of atoms, are available from the authors on request.

TABLE II. Elemental Analytical Data<sup>a</sup> and Selected Infrared Frequencies.

Complex	C(%)	H(%)	N(%)	$\nu_{C=O}$ (cm <sup>-1</sup> )
[CuL1-E]	52.90(52.57)	4.38(4.19)	15.30(15.33)	1648
[CuL2-E]·0.5CH <sub>2</sub> Cl <sub>2</sub>	50.21(50.30)	4.30(4.32)	14.64(14.64)	1658
[NiL1-E]	52.80(53.14)	4.23(4.24)	15.43(15.49)	1647
[NiL2-E]·0.5CH <sub>2</sub> Cl <sub>2</sub>	50.79(50.78)	4.32(4.36)	13.84(13.77)	1653

<sup>a</sup>Calculated values are in parentheses.

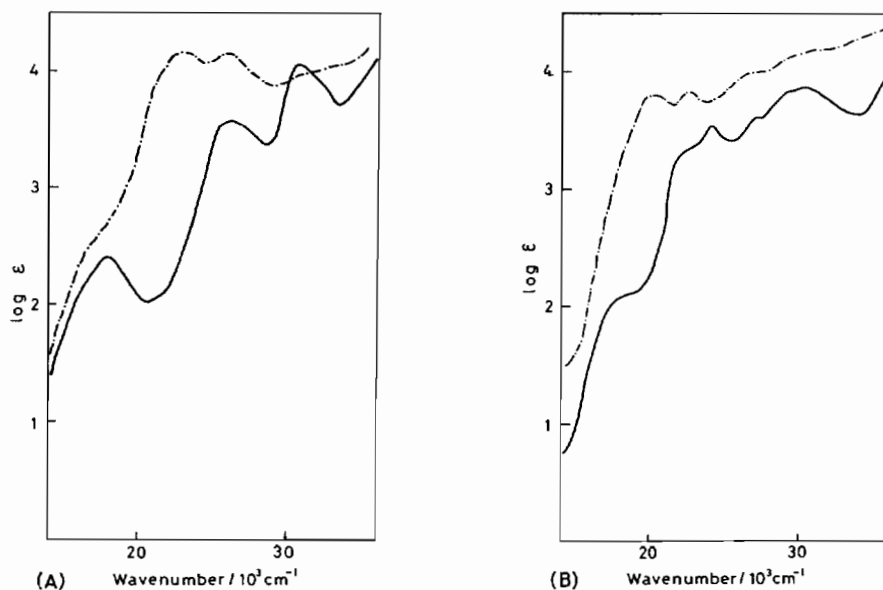


Fig. 2. (A) Electronic spectra of [CuL1-H] (—) and [CuL1-E] (---) in dichloromethane; (B) Electronic spectra of [NiL1-H] (—) and [NiL1-E] (---) in dichloromethane.

TABLE III. Bond Distances and Angles for [NiL2-E] with e.s.d.s in Parentheses.

Bond distance (Å)

Ni–O(1)	1.817(4)	C(2)–C(3)	1.341(13)
Ni–N(1)	1.879(6)	C(3)–C(4)	1.382(14)
Ni–N(2)	1.852(4)	C(4)–C(5)	1.382(8)
Ni–N(3)	1.890(6)	C(5)–C(6)	1.392(12)
O(1)–C(1)	1.295(10)	C(6)–C(7)	1.469(7)
O(2)–C(14)	1.222(9)	C(7)–C(8)	1.510(11)
O(3)–N(5)	1.217(11)	C(9)–C(10)	1.482(11)
O(4)–N(5)	1.208(10)	C(11)–C(12)	1.510(7)
N(1)–C(7)	1.280(10)	C(11)–C(13)	1.456(10)
N(1)–C(9)	1.499(6)	C(13)–C(14)	1.467(13)
N(2)–C(10)	1.481(9)	C(14)–C(15)	1.498(14)
N(2)–C(11)	1.282(11)	C(16)–C(17)	1.397(11)
N(3)–N(4)	1.312(9)	C(17)–C(18)	1.380(8)
N(3)–C(16)	1.424(6)	C(18)–C(19)	1.381(11)
N(4)–C(13)	1.324(7)	C(19)–C(20)	1.379(12)
N(5)–C(19)	1.475(7)	C(20)–C(21)	1.383(8)
C(1)–C(2)	1.430(7)	C(21)–C(16)	1.399(10)
C(1)–C(6)	1.407(10)		

Bond angle (°)

O(1)–Ni–N(1)	93.5(2)	C(1)–C(6)–C(7)	120.8(7)
O(1)–Ni–N(3)	89.1(2)	C(5)–C(6)–C(7)	121.1(6)
N(1)–Ni–N(2)	87.9(2)	N(1)–C(7)–C(6)	121.9(6)
N(2)–Ni–N(3)	89.9(2)	N(1)–C(7)–C(8)	119.7(5)
Ni–O(1)–C(1)	128.4(4)	C(6)–C(7)–C(8)	118.2(7)
Ni–N(1)–C(7)	129.4(3)	N(1)–C(9)–C(10)	109.6(5)
Ni–N(1)–C(9)	111.3(4)	N(2)–C(10)–C(9)	108.5(5)
C(7)–N(1)–C(9)	119.1(5)	N(2)–C(11)–C(12)	121.7(6)
Ni–N(2)–C(10)	109.9(4)	N(2)–C(11)–C(13)	120.0(4)
Ni–N(2)–C(11)	127.1(4)	C(12)–C(11)–C(13)	117.9(7)

(continued on facing page)

TABLE III. (continued)

C(10)–N(2)–C(11)	122.9(4)	N(4)–C(13)–C(11)	124.0(7)
Ni–N(3)–N(4)	123.9(3)	N(4)–C(13)–C(14)	112.7(6)
Ni–N(3)–C(16)	123.5(4)	C(11)–C(13)–C(14)	122.9(5)
N(4)–N(3)–C(16)	111.1(5)	O(2)–C(14)–C(13)	122.4(8)
N(3)–N(4)–C(13)	122.2(6)	O(2)–C(14)–C(15)	118.6(10)
O(3)–N(5)–O(4)	124.1(6)	C(13)–C(14)–C(15)	118.7(7)
O(3)–N(5)–C(19)	118.0(6)	N(3)–C(16)–C(17)	118.3(6)
O(4)–N(5)–C(19)	117.7(7)	N(3)–C(16)–C(21)	121.7(6)
O(1)–C(1)–C(2)	116.3(6)	C(17)–C(16)–C(21)	119.8(5)
O(1)–C(1)–C(6)	125.6(4)	C(16)–C(17)–C(18)	119.7(7)
C(2)–C(1)–C(6)	117.9(7)	C(17)–C(18)–C(19)	118.9(7)
C(1)–C(2)–C(3)	121.8(7)	N(5)–C(19)–C(18)	119.0(7)
C(2)–C(3)–C(4)	120.6(6)	N(5)–C(19)–C(20)	118.1(6)
C(3)–C(4)–C(5)	118.8(9)	C(18)–C(19)–C(20)	122.7(5)
C(4)–C(5)–C(6)	122.6(8)	C(19)–C(20)–C(21)	118.2(7)
C(1)–C(6)–C(5)	118.0(5)	C(16)–C(21)–C(20)	120.4(7)

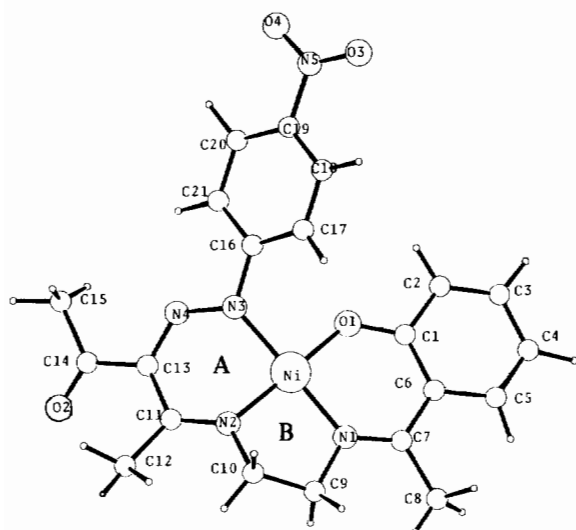


Fig. 3. A perspective drawing of [NiL1-E] with the atom numbering scheme.

coordinated by an oxygen two imine, and an azo nitrogen of the substituent moiety. One of the parent complexes, *N*-salicylaldehyde-*N'*-acetylacetonetrimethylenediaminocopper(II), was subjected to a single-crystal X-ray analysis and it was verified that the parent complex has  $N_2O_2$  donor set [4]. Therefore, it is apparent that the present substi-

tution reaction accompanies the rearrangement of the coordination sphere. The saturated five-membered chelate ring (B) has an envelope conformation, where C(9) and C(10) atoms are deviated by  $-0.12$  and  $-0.57$  Å respectively from the plane defined by Ni, N(1), and N(2), probably due to the steric effect of the neighboring two methyl groups. The chelate ring (A) takes a boat conformation, where Ni and C(13) atoms are deviated by  $0.58$  and  $0.15$  Å, respectively, from the plane defined by N(2), N(3), N(4) and C(11). It should be noted that the planarity of the acetylacetonato chelate ring of the parent complex is preserved to within  $\pm 0.04$  Å [4].

## References

- 1 J. D. Goddard, *Inorg. Nucl. Chem. Lett.*, **13**, 555 (1977).
- 2 H. A. Kuska, M. F. Farona, P. Pappas and P. Potterton, *J. Coord. Chem.*, **1**, 259 (1971).
- 3 N. Matsumoto, M. Asakawa, H. Nogami and A. Ohyoshi, *Inorg. Chim. Acta*, **96**, 87 (1985).
- 4 N. Matsumoto, M. Asakawa, H. Nogami, M. Higuchi and A. Ohyoshi, *J. Chem. Soc., Dalton Trans.*, in press.
- 5 'International Tables for X-Ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1974.
- 6 T. Sakurai and K. Kobayashi, 'Manual for UNICS III System', Rikagakukenyusho, 1978.
- 7 S. Kawano, *Kohou Comp. Cent. Kyushu Univ.*, **16**, 113 (1983).