

Ambidentate Ligand의 금속 착물 (제1보). Isonitrosobenzoylacetone Imine 유도체와 니켈(II)의 착물

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Metal Complexes of Ambidentate Ligands (I). Nickel(II) Complexes of Isonitrosobenzoylacetone Imine Derivatives

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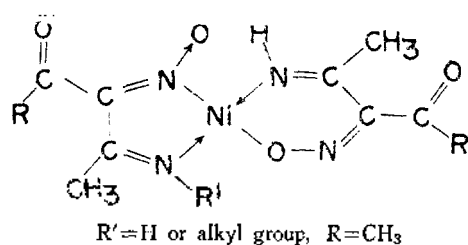
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요 약. Ambidentate 리간드인 isonitrosobenzoylacetone imine 및 그 N-알킬치환체들의 새로운 니켈(II) 착물 Ni(IBA-NH)(IBA-NR)를 합성하였다. 여기서 IBA-NH 및 IBA-NR (R=H, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl 또는 benzyl)은 각각 isonitrosobenzoylacetone imine 및 그 N-알킬치환체를 표시한다. 합성한 니켈(II) 착물들의 적외선, 핵자기공명, 전자스펙트럼 및 자기모멘트 등을 측정된 결과 이들 착물에서 IBA-NH 리간드는 이소니트로소기의 산소를 통하여 니켈에 배위되어 6각형 고리를 이루고 있으며, 그리고 IBA-NR 리간드는 이소니트로소기의 질소를 통하여 니켈에 배위되어 5각형 고리를 이루고 있음을 확인하였다. 이들 리간드의 배위 구조는 Bose 등⁵에 의해 알려진 isonitrosoacetylacetone imine 및 N-알킬유도체들의 구조와 유사하다.

ABSTRACT. Novel nickel(II) complexes of the type Ni(IBA-NH)(IBA-NR), where IBA-NH and IBA-NR (R=H, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl or benzyl) represent isonitrosobenzoylacetone imine and its *N*-alkyl derivative respectively, have been prepared. The ir, nmr, and electronic spectra and magnetic moment of the nickel(II) complexes have been studied. It has been determined that the isonitroso group of IBA-NH coordinates to nickel through the oxygen to form 6-membered chelate ring and that of IBA-NR coordinates to nickel through the nitrogen to form 5-membered ring in square-planar Ni(IBA-NH)(IBA-NR). The coordination manner of the ligands is similar to that of isonitrosoacetylacetone imines obtained by Bose, *et al.*⁵

INTRODUCTION

The isonitroso derivatives of benzoylactone are particularly interesting, because the isonitroso group has two probable coordinating sites in forming bonds with metal ions. The transition metal complexes of isonitrosoacetylacetone imines have been widely prepared and their structures have been assigned.¹⁻⁵ Among these assignments Lacey *et al.*⁴ and Bose *et al.*⁵ reported that (isonitrosoacetylacetone imino) (N-alkyl isonitrosoacetylacetone imino) nickel(II) complexes has the following structure:



In this structure the isonitroso group of isonitrosoacetylacetone imine coordinates through the oxygen and that of N-alkyl isonitrosoacetylacetone imine through the nitrogen, competing with the imine group to form bonds with nickel ion.

On the other hand it will be of interest to see if the coordination manner of those ligands is similar to that obtained by Bose *et al.*⁵ when a bulkier phenyl group is substituted for methyl group in R of the ligands.

The transition metal complexes of isonitrosobenzoylacetone imines which have four donor atoms and can also behave as versatile ambidentate ligands have not been studied. The present paper deals with the preparation and structural characterization of new nickel(II) complexes with isonitrosobenzoylacetone imine and its N-alkyl derivatives.

EXPERIMENTAL

Materials Used. Benzoylacetone was prepared

from Claisen condensation of acetophenone and ethylacetate by published method⁶.

Except for *n*-propyl amine, *iso*-propylamine and *n*-butyl amine all other amines used were in aqueous solutions. Other reagents used were commercially available reagent grade.

Methods and Apparatus. The magnetic susceptibilities of the nickel(II) complexes were measured (at room temperature) by the Faraday method using HgCo(NCS)₄ as a calibrant⁷ and diamagnetic corrections were made using Pascal's constants. The electronic spectra of the complexes in chloroform solution were recorded on a Cary 14 UV-VIS spectrophotometer.

The infrared spectra of the compounds in Nujol mulls were recorded on a Beckman IR-12 spectrophotometer. The proton nuclear magnetic resonance spectra of the compounds in CDCl₃ solution were recorded on a Varian HA-100 D spectrometer, using tetramethylsilane as the internal reference.

Preparations

(1) Isonitrosobenzoylacetone: This was prepared by nitrosation of benzoylacetone with sodium nitrite. In a solution of benzoylacetone (48.6 g, 0.30 mole) and sodium hydroxide (12 g, 0.30 mole) in 250 ml of water, sodium nitrite (21.7 g, 0.315 mole) was dissolved.

Then the solution was cooled to 0~5 °C and was added slowly 300 ml of 10 % sulfuric acid with stirring. After stirring for 2 hrs more the white precipitate formed was filtered, washed with water and dried over P₂O₅; yield 40.0 g (70 %), m. p 116 °C.

Anal. Calcd for C₁₀H₉NO₃: C 62.8; H 4.71; N 7.33.

Found: C 63.0; H 4.57; N 7.37.

(2) *bis*(Isonitrosobenzoylacetone imino) nickel(II), Ni(IBA-NH)(IBA-NH): Nickel chloride hexahydrate (1.2 g, 0.05 mole) and isonitrosobenzoylacetone (1.9 g, 0.01 mole) were dissolved

in 25 ml of ethanol, and 3 ml of 30 % ammonia water was added to it. After reflux over a water bath for 2 hrs the solution was evaporated under vacuum until crystals were formed. The orange-yellow crystals formed were filtered off, washed with small amounts of ethanol and recrystallized from chloroform yield 1.8g (82%).

Anal. Calcd. for $\text{NiC}_{20}\text{H}_{18}\text{N}_4\text{O}_4$: C 55.0; H 4.12; N 12.8.

Found: C 55.3; H 4.00; N 12.5.

(3) (Isonitrosobenzoylacetone imino)(N-methylisonitrosobenzoylacetone imino)nickel(II), $\text{Ni}(\text{IBA-NH})(\text{IBA-NMe})$. To a solution of $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$ (0.44 g; 0.001 mole) in 2 ml of ethanol and chloroform (3 : 2) mixture, methylamine (1 ml, 30 %, 0.01 mole) was added.

The reaction mixture was refluxed for 3 hrs. The solution was evaporated under vacuum until crystals were formed. The yellow crystals were filtered off, washed with small amount of ethanol, and recrystallized from ethanol; yield 0.31 g (69 %).

Anal. Calcd. for $\text{NiC}_{21}\text{H}_{20}\text{N}_4\text{O}_4$: C 55.9; H 4.44; N 12.4.

Found: C 56.0; H 4.32; N 12.6.

(4) (Isonitrosobenzoylacetone imino)(N-ethylisonitrosobenzoylacetone imino)nickel(II), $\text{Ni}(\text{IBA-NH})(\text{IBA-NEt})$: This was produced by the same method as that for $\text{Ni}(\text{IBA-NH})(\text{IBA-N})$ except that $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$ (0.44 g, 0.001 mole) and ethylamine (0.7 ml, 70 %, 0.01 mole) in 25 ml of chloroform and ethanol (2:1) mixture were refluxed over a water bath for 5 hrs. The orange-yellow crystals obtained were recrystallized from ethanol; yield 0.32 g (74 %).

Anal. Calcd. for $\text{NiC}_{22}\text{H}_{22}\text{N}_4\text{O}_4$: C 56.8; H 4.75; N 12.1.

Found: C 56.6; H 4.66; N 12.3.

(5) (Isonitrosobenzoylacetone imino)(N-*n*-

propylisonitrosobenzoylacetone imino)nickel(II) $\text{Ni}(\text{IBA-NH})(\text{IBA-Nn-Pr})$; $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$ (0.44 g, 0.001 mole) and *n*-propylamine (0.6 ml, 0.01 mole) in 25 ml of ethanol and chloroform (3 : 2) mixture were refluxed over a water bath for 3 hrs. The rest of the procedure was the same as in section (3). The brown crystals obtained were recrystallized from ethanol; yield 0.35 g (73 %).

Anal. Calcd. for $\text{NiC}_{23}\text{H}_{24}\text{N}_4\text{O}_4$: C 57.7; H 5.0; N 11.7.

Found: C 57.4; H 5.05; N 11.9.

(6) (Isonitrosobenzoylacetone imino)(N-isopropylisonitrosobenzoylacetone imino)nickel(II), $\text{Ni}(\text{IBA-NH})(\text{IBA-Ni-Pr})$: $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$ (0.88 g, 0.002 mole) and isopropylamine (3.5 ml, 0.05 mole) in 50 ml of isopropyl alcohol were refluxed over a water bath for 10 hrs. The rest of procedure was the same as in section (3). The orange-yellow crystals obtained were recrystallized from ethanol; yield 0.40 g (42 %).

Anal. Calcd. for $\text{NiC}_{23}\text{H}_{24}\text{N}_4\text{O}_4$: C 57.7; H 5.01; N 11.7.

Found: C 56.8; H 5.05; N 11.2.

(7) (Isonitrosobenzoylacetone imino)(N-*n*-butylisonitrosobenzoylacetone imino)nickel(II), $\text{Ni}(\text{IBA-NH})(\text{IBA-Nn-Bu})$. $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$ (0.66 g, 0.0015 mole) and *n*-butylamine (1.0 ml, 0.015 mole) in 37 ml of ethanol and chloroform (3:2) mixture were refluxed over a water bath for 5 hrs. The rest of procedure was the same as in section (3). The brown crystals obtained were recrystallized from ethanol; yield 0.41 g, (54 %).

Anal. Calcd. for $\text{NiC}_{24}\text{H}_{26}\text{N}_4\text{O}_4$: C 58.5; H 5.28; N 11.4.

Found: C 58.2; H 5.14; N 11.4.

(8) (Isonitrosobenzoylacetone imino)(N-benzylisonitrosobenzoylacetone imino)nickel(II), $\text{Ni}(\text{IBA-NH})(\text{IBA-NBz})$: $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$

NH) (0.44 g, 0.001 mole) and benzylamine (0.9 ml, 0.01 mole) in 25 ml of ethanol and chloroform (3:2) mixture were refluxed over a water bath for 5 hrs. The rest of procedure was the same as in section (3). The brown crystals obtained were recrystallized from ethanol; yield 0.32 g (59%).

Anal. Calcd. for $\text{NiC}_{25}\text{H}_{22}\text{N}_4\text{O}_4$: C 62.1; H 4.81; N 10.4.

Found: C 61.8; H 4.78; N 10.7.

RESULTS AND DISCUSSION

Preparation of Nickel Complexes. All the spectroscopic and analytical data are consistent with the structural assignment of isonitrosobenzoylacetone prepared. This compound is not soluble in water but in most polar organic solvents (ethanol, chloroform, etc.) In the preparation of alkyl substituted nickel(II) complex, $\text{Ni}(\text{IBA-NH})(\text{IBA-NR})$, from $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$ a large excess (about 10 times greater than required in most cases) of amine was used so as to facilitate the amine-exchange reaction. The steric hindrance seems to influence the amine-exchange reaction, as the reactions with isopropylamine and benzylamine were comparatively difficult. Both amines are bulkier than other amines used in size. In the above amine-exchange reaction the bisalkyl substituted nickel(II) complex, $\text{Ni}(\text{IBA-NR})(\text{IBA-NR})$, where R is an alkyl group, is not formed at all. The nonreactivity of one ligand in $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$ to form $\text{Ni}(\text{IBA-NR})(\text{IBA-NH})$ may be due to the difference in the electronic configurations or in the steric interactions between the ligands. The attempts to prepare $\text{Ni}(\text{IBA-NR})(\text{IBA-NR})$ by direct reaction of nickel ion with isonitrosobenzoylacetone and alkyl amine was failed. It is expected that $\text{Ni}(\text{IBA-NR})(\text{IBA-NR})$ is unstable due to the steric interaction between the projecting N-O and N-R groups in *cis* posi-

tions. The same factor can be also accounted for the nonreactivity of one isonitrosobenzoylacetone imine toward alkylamines in $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$ ⁵.

Structure of Nickel Complexes. All the nickel(II) complexes are diamagnetic, indicating their square-planar stereochemistry. The electronic spectra (Table 1) of the nickel(II) complexes in chloroform in the region $40000\sim 8000\text{ cm}^{-1}$ are very similar each other, indicating their close structural similarity. All the spectra show strong absorption bands at $33\sim 40\text{ kK}$ ($\epsilon\sim 10^4$), which is assigned to $\pi\rightarrow\pi^*$ transition in the ligand. The charge transfer band is observed near 29 kK ($\epsilon\sim 10^3$). The nickel(II) complexes reveal also weak band at $20\sim 22\text{ kK}$ ($\epsilon\sim 10^2$). The position and intensity of these bands suggest that it may be assigned to the spin allowed d-d transition, ${}^1A_{1g}\rightarrow{}^1A_{2g}$, in the square planar nickel(II) complexes.

The ir spectra (Table 2) of $\text{Ni}(\text{IBA-NH})(\text{IBA-NR})$ in Nujol in the region $4000\sim 300\text{ cm}^{-1}$ are also closely similar each other. The strong absorption bands occurring at $1665\sim 1667$ and $1655\sim 1662\text{ cm}^{-1}$ are assigned to two coordinated carbonyl groups. Although the spectrum of $\text{Ni}(\text{IBA-NH})(\text{IBA-NH})$ shows two N-H stretching bands at 3285 and 3272 cm^{-1} , those of other complexes show only one N-H stretching band at $3160\sim 3180\text{ cm}^{-1}$. The disappearance of one band is attributed to the replacement of one of the two N-H hydrogens by an alkyl group in $\text{Ni}(\text{IBA-NH})(\text{IBA-NR})$ (R=alkyl group). The spectra of the nickel(II) complexes show a strong band at $1165\sim 1167\text{ cm}^{-1}$ that can be assigned to the nitrogen-coordinated N-O stretching frequency. The oxygen coordinated N-O stretching band will be appeared at lower frequency but can not be assigned certainly due to the overlapping of aromatic bands.

In agreement with ir data the nmr spectrum

Table 1. Electronic spectral bands of nickel(II) complexes.

Complexes	Absorption max. (ϵ , mol ⁻¹ cm ⁻¹)			
Ni(IBA-NH)(IBA-NH)	39.5(-10 ⁴)	33.3(-10 ⁴)	29.0(-10 ³)	20.0(-10)
Ni(IBA-NH)(IBA-NMe)	39.5(-10 ⁴)	33.3(-10 ⁴)	29.0(-10 ³)	22.5(-10)
Ni(IBA-NH)(IBA-NEt)	38.5(-10 ⁴)	33.3(-10 ⁴)	29.0(-10 ³)	22.5(-10)
Ni(IBA-NH)(IBA-Nn-Pr)	38.5(-10 ⁴)	33.9(-10 ⁴)	28.8(-10 ³)	22.7(-10)
Ni(IBA-NH)(IBA-Ni-Pr)	38.8(-10 ⁴)	33.3(-10 ⁴)	29.1(-10 ³)	24.0(-10)
Ni(IBA-NH)(IBA-Nn-Bu)	38.9(-10 ⁴)	33.3(-10 ⁴)	29.4(-10 ³)	22.2(-10)
Ni(IBA-NH)(IBA-NBz)	39.5(-10 ⁴)	33.3(-10 ⁴)	28.8(-10 ³)	20.0(-10)

Table 2. Important infrared bands of Ni(II) Complexes (cm⁻¹)

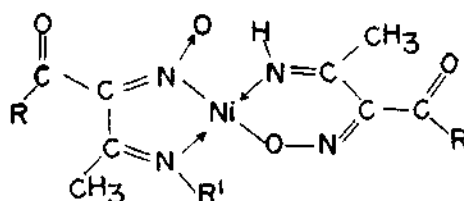
Complexes	N-H str.	C=O str.	N-O (N-coord.) str.
Ni(IBA-NH)(IBA-NH)	3285 _m , 3272 _m	1672 _{vs} , 1657 _{vs}	1188
Ni(IBA-NH)(IBA-NMe)	3165 _w	1657 _{vs}	1230 _s
Ni(IBA-NH)(IBA-NEt)	3175 _w	1663 _{vs}	1230 _s
Ni(IBA-NH)(IBA-Nn-Pr)	3160 _w	1660 _{vs}	1175 _m
Ni(IBA-NH)(IBA-Ni-Pr)	3180	1656 _{vs}	1230 _s
Ni(IBA-NH)(IBA-Mn-Bu)	3160 _w	1653 _{vs}	1190 _s
Ni(IBA-NH)(IBA-NBz)	3170 _w	1665 _{vs}	1192 _s

vs, very strong; *s*, strong; *m*, medium; *w*, weak.

of Ni(IBA-NH)(IBA-NH) in CDCl₃ show two N-H proton signals at δ 7.8 and 8.79 ppm, but other nickel complexes give only one N-H proton signal around 9.0 ppm because of an alkyl substitution. In the nmr spectrum of Ni(IBA-NH)(IBA-NR), two proton signals at δ 2.13~2.20 and 2.38~2.42 ppm are due to the existence of two nonequivalent methyl groups in the complexes. The proton signal of NOH group, which is observed at δ 8.8 ppm in the spectrum of isonitrobenzoylacetone, is missed in the spectra of nickel(II) complexes. This leads to the conclusion that the hydrogen atom of the NOH group is replaced by nickel ion to form the complexes.

Assuming that the imino nitrogen remain always coordinated to nickel ion, the ligand can use either the carbonyl group or the isonitroso group (both oxygen and nitrogen are potential donors) to occupy the remaining coordinating positions of the nickel ion. From the

above results it is suggested that Ni(IBA-NH)(IBA-NH) have the following square-planar structure, in which isonitrosobenzoylacetone imine is expected to coordinate to nickel ion through the isonitroso oxygen forming 6-membered chelate ring and N-alkylisonitrosobenzoylacetone imine to coordinate to nickel ion through the isonitroso nitrogen forming 5-membered chelate ring.



R' = H or alkyl group, R = phenyl group

Mainly due to the introduction of a bulkier phenyl group a slightly different coordination manner of the ligand from that of isonitroso-

Table 3. Proton nuclear magnetic resonance signals of nickel(II) complexes (δ , ppm).

Complexes	N—H	=C—CH ₃		N—R
Ni(IBA-NH)(IBA-NH)	7.8, 8.79	2.13	2.38	
Ni(IBA-NH)(IBA-NMe)	8.95	2.17	2.39	3.14(CH ₃)
Ni(IBA-NH)(IBA-NEt)	9.02	2.20	2.41	1.29 t (CH ₃), 3.55 q (CH ₂)
Ni(IBA-NH)(IBA-Nn-Pr)	8.95	2.17	2.37	1.01 t (CH ₃), 1.73 s (CH ₂) 2.46 t (CH ₂)
Ni(IBA-NH)(IBA-Ni-Pr)	9.02	2.15	2.38	1.51(CH ₃), 4.18 h (CH)
Ni(IBA-NH)(IBA-Nn-Bu)	8.99	2.18	2.38	1.00 d (CH ₃) 1.6 m (CH ₂) 3.49 t (CH ₂)
Ni(IBA-NH)(IBA-NBz)	9.04	2.17	2.42	4.78(CH ₂), 5(C ₆ H ₅)

d , doublet; t , triplet; q , quartet; s , sextet; h , heptuplet, m , multiplet.

acetylacetone was expected. However, it has turned out that the coordination manner of the isonitrosobenzoylacetone imines is identical to that of the isonitrosoacetylacetone obtained by Bose *et al.*⁵ in nickel(II) complexes.

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