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Synthesis, Characterization, and Crystal-structure Analysis of the 2 : 1 Molecular Complexes between 1,3,5-Trinitrobenzene and Copper(II), Nickel(II), or Palladium(II) Complexes with the Schiff Base Ligands Derived from *o*-Hydroxynaphthaldehydes and Monoamines

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The molecular complexes between 1,3,5-trinitrobenzene(TNB) and copper(II), nickel(II), or palladium(II) complexes with the Schiff base ligands derived from 1-hydoxy-2-naphthaldehyde or 2-hydroxy-1-naphthaldehyde and monoamines (RNH$_2$: R=CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, i-C$_3$H$_7$, n-C$_4$H$_9$) have been prepared and characterized. One of the molecular complexes bis(1-(isopropyliminomethyl)-2-naphtholato)palladium(II)-bis(1,3,5-trinitrobenzene) (Pd(2,1-i-C$_3$H$_7$)$_2$·2TNB) has been subjected to the single-crystal X-ray analysis. Its crystal structure consists of alternately stacked donor (naphthalene moiety of the metal complex) and acceptor (TNB) molecules. The coordination geometry is a square planar with a markedly stepped chair-like shape, where the seat and the rests are formed by the coordination plane (PdO$_2$N$_2$) and two naphthalene moieties. The Pd atom is deviated by 0.62 Å from the least-squares plane of the naphthalene ring and the dihedral angle between the coordination plane and the naphthalene ring is 25.1°. When the crystal structure was viewed perpendicular to the donor or acceptor plane, the center of the TNB molecule coincides approximately the center of terminal benzene ring of the naphthalene moiety. Electronic spectra of the molecular complexes in Nujol mull showed a new band at about 18×10^3 cm^{-1}, which was not observed in solution spectra.

Previously[1,2] we have studied the 2:1 molecular complexes between TCNQ and the Schiff base metal complexes **1** or **2**, in order to investigate the structure of the molecular complex in which both the π–π type donor-acceptor interaction and the steric hindrance of the N-substituted alkyl group causing a tetrahedral distortion of the coordination geometry are operating simultaneously, where the abbreviations of the compounds are shown in Fig. 1. The results indicated that the donor-acceptor interaction can affect the coordination geometry and the steric hindrance between two neighboring acceptor molecules lied on the naphthalene moieties of the complex as well as the overlapping mode between donor and acceptor molecules is important for the formation of the molecular complex. TNB molecule takes C_{3v} symmetry, while TCNQ takes D_{2h} symmetry. Based on preliminary molecular model consideration, TNB molecule seems to be sterically much favorable for the formation of the molecular complex with **1** or **2** than TCNQ, although TNB is a weaker π-electron acceptor than TCNQ. In this study, TNB instead of TCNQ was used to examine whether the complexes **1** or **2** can form the molecular complexes with TNB. One of the molecular complexes with TNB, Pd(2,1-i-C$_3$H$_7$)$_2$·2TNB has been subjected to the single-crystal X-ray analysis, in order to confirm the basic structure for a series of the molecular complexes with TNB and compare the overlapping mode of TNB adduct with that of TCNQ adduct.

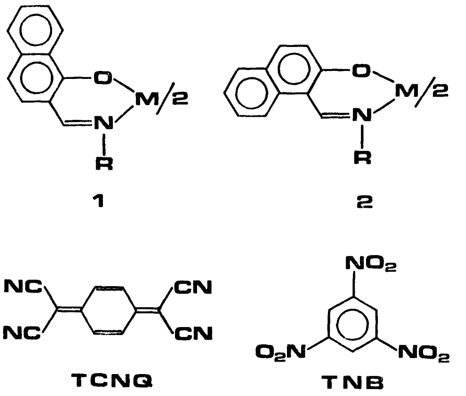

Fig. 1. Structures of Schiff base metal complexes **1** and **2**, and 7,7,8,8-tetracyanoquinodimethane (TCNQ), and 1,3,5-trinitrobenzene (TNB). Bis(2-(alkyliminomethyl)-1-naphtholato)metal(II) (**1**) and bis(1-(alkyliminomethyl)-2-naphtholato)metal(II) (**2**) are abbreviated as M(1,2-R)$_2$ and M(2,1-R)$_2$, respectively, where M and R denote metal ion and alkyl group, respectively.

Experimental

Physical Measurements. Elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. Electronic spectra were measured on a Shimadzu UV-200 spectrometer in Nujol mull and on a Hitachi recording spectrophotometer 323 in acetone-chloroform solution. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGC-20 type microthermobalance at the heating rate of 5 °C min^{-1}. Differential scanning calorimetry (DSC) was carried out on a Shimadzu DT-20Bs and DSC-20 and the calibration was made by the use of Indium metal.

Syntheses. 1-Hydroxy-2-naphthaldehyde was prepared by the method of Weil and Ostermeier.[3] 2-Hydroxy-1-naphthaldehyde was purchased from Tokyo Chemical Industry Co., Ltd.

Parent Complexes 1 and 2. Bis(1-(alkyliminomethyl)-2-naphtholato)copper(II), -nickel(II), and -palladium(II) were prepared by the method of Chakravorty and Holm[4] from the Schiff base reaction of bis(1-formyl-2-phtholato)-coppor(II), -nickel(II), and -palladium(II) with monoamines, where the complexes are abbreviated as M(2,1-R)$_2$ (M=Cu^{2+}, Ni^{2+}, Pd^{2+}; R=CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, i-C$_3$H$_7$, n-C$_4$H$_9$, i-C$_4$H$_9$, s-C$_4$H$_9$, t-C$_4$H$_9$). Bis(2-(alkyliminomethyl)-1-naphtholato)copper(II) was also prepared according to the literature[4] and abbreviated as Cu(1,2-R)$_2$ (R=CH$_3$, C$_2$H$_5$,

Table 1. Final atomic parameters of $Pd(2,1\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$. The atomic parameters have been multiplied by 10^4

Atom	x	y	z	$B_{eq}/Å^2$
Pd	0	0	0	1.5
O(1)	853(3)	581(9)	1603(5)	2.2
N(1)	405(4)	1992(10)	−453(6)	1.8
C(1)	1692(5)	2207(13)	1401(7)	1.8
C(2)	1517(5)	1340(13)	2037(7)	1.9
C(3)	2070(5)	1302(15)	3203(7)	2.4
C(4)	2797(6)	1998(15)	3739(8)	2.7
C(5)	3031(5)	2734(13)	3133(8)	2.4
C(6)	3841(5)	3303(15)	3713(8)	3.0
C(7)	4064(6)	3934(14)	3128(9)	3.1
C(8)	3513(6)	4052(15)	1971(8)	2.8
C(9)	2738(5)	3522(14)	1385(8)	2.6
C(10)	2480(5)	2872(13)	1961(7)	2.0
C(11)	1123(5)	2606(13)	244(7)	1.9
C(12)	−145(5)	2786(14)	−1584(7)	2.1
C(13)	−623(6)	4264(16)	−1576(9)	3.6
C(14)	256(6)	3508(16)	−2012(8)	2.8
O(2)	2654(6)	−3078(16)	3895(8)	7.8
O(3)	3922(5)	−2953(15)	5070(7)	6.7
O(4)	5290(4)	−580(14)	3859(7)	6.3
O(5)	4648(4)	506(12)	2187(7)	5.0
O(6)	1817(4)	−266(14)	−431(6)	5.1
O(7)	1384(5)	−2505(14)	−43(7)	6.7
N(2)	3285(6)	−2753(14)	4162(8)	4.6
N(3)	4699(5)	−269(15)	2925(8)	4.2
N(4)	1872(5)	−1421(14)	169(7)	3.9
C(15)	3284(6)	−2128(15)	3237(8)	3.1
C(16)	3987(6)	−1527(14)	3508(8)	2.9
C(17)	3957(6)	−941(15)	2656(9)	2.9
C(18)	3276(6)	−843(15)	1554(8)	2.9
C(19)	2601(6)	−1496(15)	1331(8)	2.9
C(20)	2586(6)	−2122(14)	2149(8)	2.8

$n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_4H_9$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$). The parent complexes are identified by their elemental analyses and melting points.[5)]

Molecular Complexes with TNB. The method for the preparation of the molecular complexes is practically the same and exemplified by the synthesis of $Pd(2,1\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$. A solution of $Pd(2,1\text{-}i\text{-}C_3H_7)_2$ (5 mmol) in 20 cm^3 of dichloromethane is added to a solution of TNB (10 mmol) in 20 cm^3 of acetone. The solution was warmed at 40 °C for 5 min in a water bath, which on standing overnight in a refrigerator precipitated red needle crystals. They were collected and dried *in vacuo*. The other molecular complexes were prepared under the same reaction condition described above.

X-Ray Analysis of $Pd(2,1\text{-i-}C_3H_7)_2\cdot 2TNB$*.* Red needle crystals were prepared by slow precipitation of an equivolume solution of dichloromethane and acetone at room temperature. A crystal with approximate dimensions of $0.2\times0.3\times0.5$ mm^3 was used for the X-ray diffraction study. The unit cell parameters and intensity data were measured on a Rigaku Denki AFC-5 automated four-circle diffractometer with a graphite monochromatized Mo $K\alpha$ radiation at 20 ± 1 °C. The unit cell parameters were determined by the least-squares method based on 20 reflections in the range of $18°<2\theta<28°$. Crystal data: $PdO_{14}N_8C_{40}H_{34}$, F.W.=957.2, monoclinic, space group $P2_1/c$, $a=22.236(7)$, $b=7.255(1)$, $c=15.584(4)$ Å, $\beta=129.66(1)°$, $V=1935.2(10)$ $Å^3$, $D_m=1.63$ (by flotation method in aqueous KI solution), $D_x=1.643$ g cm^{-3} ($Z=2$), and $\mu=3.8$ cm^{-1} (Mo $K\alpha$).

Intensity data were collected by the $\theta-2\theta$ scan technique with a scan rate of 8° min^{-1}. For weak reflections the peak scan was repeated up to three times depending on their intensities. Three check reflections were monitored every 100 reflections throughout the set and displayed no decay of intensities. A total of 3392 independent reflections with $1.5°<2\theta<48°$ were collected, of which 2601 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure analysis. Lorentz and polarization corrections were applied, but no correction for absorption was made because of the crystal size and low absorption coefficient.

Table 2. Elemental analyses of molecular complexes

Complex	Found (Calcd) (%)		
	C	H	N
$Cu(2,1\text{-}CH_3)_2\cdot 2TNB$	50.14(50.38)	3.03(3.05)	12.89(13.06)
$Cu(2,1\text{-}C_2H_5)_2\cdot 2TNB$	51.43(51.50)	3.41(3.41)	12.70(12.64)
$Cu(2,1\text{-}n\text{-}C_3H_7)_2\cdot 2TNB$	52.33(52.55)	3.66(3.75)	12.28(12.26)
$Cu(2,1\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$	52.55(52.55)	3.66(3.75)	12.18(12.26)
$Cu(2,1\text{-}n\text{-}C_4H_9)_2\cdot 2TNB$	53.43(53.53)	4.03(4.06)	11.75(11.89)
$Ni(2,1\text{-}CH_3)_2\cdot 2TNB$	50.65(50.67)	3.08(3.07)	13.10(13.13)
$Ni(2,1\text{-}C_2H_5)_2\cdot 2TNB$	51.86(51.78)	3.43(3.43)	12.75(12.71)
$Ni(2,1\text{-}n\text{-}C_3H_7)_2\cdot 2TNB$	52.56(52.83)	3.77(3.77)	12.36(12.32)
$Ni(2,1\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$	52.81(52.83)	3.69(3.77)	12.33(12.32)
$Ni(2,1\text{-}n\text{-}C_4H_9)_2\cdot 2TNB$	53.83(53.81)	4.09(4.09)	11.94(11.95)
$Pd(2,1\text{-}n\text{-}C_3H_7)_2\cdot 2TNB$	50.20(50.19)	3.51(3.58)	11.76(11.71)
$Pd(2,1\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$	50.17(50.19)	3.50(3.58)	11.76(11.71)
$Pd(2,1\text{-}n\text{-}C_4H_9)_2\cdot 2TNB$	51.17(51.20)	3.83(3.89)	11.34(11.37)
$Cu(1,2\text{-}n\text{-}C_3H_7)_2\cdot 2TNB$	52.44(52.55)	3.70(3.75)	12.25(12.26)
$Cu(1,2\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$	52.32(52.55)	3.69(3.75)	12.27(12.26)
$Cu(1,2\text{-}n\text{-}C_4H_9)_2\cdot 2TNB$	53.12(53.53)	3.91(4.06)	11.93(11.89)

TABLE 3. BOND DISTANCES AND ANGLES WITH THEIR ESTIMATED STANDARD DEVIATIONS FOR 1:2 MOLECULAR ADDUCT BETWEEN BIS(1-(ISOPROPYLIMINOMETHYL)-2-NAPHTHOLATO)PALLADIUM(II) AND 1,3,5-TRINITROBENZENE

Bond distance	l/Å	Bond distance	l/Å	Bond distance	l/Å	Bond distance	l/Å
Bis(1-(isopropyliminomethyl)-2-naphtholato)-palladium(II)				1,3,5-Trinitrobenzene			
Pd-O(1)	1.991(8)	C(7)-C(8)	1.39(1)	N(2)-O(2)	1.20(1)	C(17)-C(18)	1.38(1)
Pd-N(1)	2.054(9)	C(8)-C(9)	1.39(1)	N(2)-O(3)	1.21(1)	C(18)-C(19)	1.39(1)
O(1)-C(2)	1.29(1)	C(9)-C(10)	1.41(1)	N(2)-C(15)	1.51(1)	C(19)-N(4)	1.47(1)
C(2)-C(1)	1.42(1)	C(10)-C(1)	1.45(1)	C(15)-C(16)	1.40(1)	N(4)-O(6)	1.20(1)
C(2)-C(3)	1.40(1)	C(1)-C(11)	1.42(1)	C(16)-C(17)	1.35(1)	N(4)-O(7)	1.20(1)
C(3)-C(4)	1.36(1)	C(11)-N(1)	1.30(1)	C(17)-N(3)	1.50(1)	C(19)-C(20)	1.37(1)
C(4)-C(5)	1.44(1)	N(1)-C(12)	1.47(1)	N(3)-O(4)	1.20(1)	C(20)-C(15)	1.38(1)
C(5)-C(6)	1.46(1)	C(12)-C(13)	1.51(1)	N(3)-O(5)	1.21(1)		
C(5)-C(10)	1.41(1)	C(12)-C(14)	1.50(1)				
C(6)-C(7)	1.36(1)						

Bond angle	ϕ/°	Bond angle	ϕ/°
Bis(1-(isopropyliminomethyl)-2-naphtholato)palladium(II)			
N(1)-Pd-O(1)	90.3(3)	C(9)-C(10)-C(1)	123(1)
Pd-O(1)-C(2)	127.1(7)	C(9)-C(10)-C(5)	118(1)
O(1)-C(2)-C(3)	115(1)	C(5)-C(10)-C(1)	118(1)
O(1)-C(2)-C(1)	123(1)	C(10)-C(1)-C(11)	116.6(9)
C(1)-C(2)-C(3)	120(1)	C(10)-C(1)-C(12)	119(1)
C(2)-C(3)-C(4)	120(1)	C(2)-C(1)-C(11)	123(1)
C(3)-C(4)-C(5)	121(1)	C(1)-C(11)-N(1)	127(1)
C(4)-C(5)-C(6)	121(1)	C(11)-N(1)-C(12)	119.9(9)
C(4)-C(5)-C(10)	119(1)	C(11)-N(1)-Pd	121.6(7)
C(10)-C(5)-C(6)	119(1)	Pd-N(1)-C(12)	118.3(7)
C(5)-C(6)-C(7)	120(1)	N(1)-C(12)-C(13)	108.4(9)
C(6)-C(7)-C(8)	119(1)	N(1)-C(12)-C(14)	113.0(9)
C(7)-C(8)-C(9)	121(1)	C(13)-C(12)-C(14)	111(1)
C(8)-C(9)-C(10)	120(1)		
1,3,5-Trinitrobenzene			
C(20)-C(15)-C(16)	121(1)	C(17)-N(3)-O(5)	117(1)
C(20)-C(15)-N(2)	119(1)	O(4)-N(3)-O(5)	126(1)
N(2)-C(15)-C(16)	118(1)	C(17)-C(18)-C(19)	116(1)
C(15)-N(2)-O(2)	115(1)	C(18)-C(19)-C(20)	122(1)
C(15)-N(2)-O(3)	115(1)	C(18)-C(19)-N(4)	117(1)
O(2)-N(2)-O(3)	127(1)	N(4)-C(19)-C(20)	119(1)
C(15)-C(16)-C(17)	117(1)	C(19)-N(4)-O(6)	117(1)
C(16)-C(17)-C(18)	124(1)	C(19)-N(4)-O(7)	113(1)
C(16)-C(17)-N(3)	118(1)	O(6)-N(4)-O(7)	128(1)
N(3)-C(17)-C(18)	117(1)	C(19)-C(20)-C(15)	117(1)
C(17)-N(3)-O(4)	115(1)		

Structure Determination. The Pd atom is required to lie at an inversion center from the consideration of the space group and the number of the formula unit in the unit cell. A Fourier synthesis based on the Pd atom revealed all the nonhydrogen atoms. Block-diagonal least-squares refinement was calculated by initially isotropic thermal parameters and the anisotropic ones, where the function minimized was $\sum w(|F_o|-k|F_c|)^2$ and $w=1/\sigma(|F_o|)^2$. At this stage, a difference Fourier synthesis was calculated and located all the hydrogen atoms at the chemically reasonable positions. Further refinement including the hydrogen atoms with anisotropic thermal parameters for nonhydrogen atoms and isotropic ones for hydrogen atoms was calculated to give final discrepancy indices of 6.26 and 6.95% for $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, respectively. A final difference Fourier synthesis showed no regions of significant electron density (less than 0.5 e Å^{-3}).

The neutral atomic scattering factors for H, C_{cov}, N, O, and Pd were taken from International Tables for X-Ray Crystallography, Vol. IV.[6] Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for all the component atoms were also taken from the literature.[6] All the calculations were carried out on a FACOM M-200 computer at the Computer Center of Kyushu University by the use of local version[7] of the UNICS II Crystallographic Computing System.[8] Final positional parameters with their estimated standard deviations are given in Table 1. Lists of structure factors and anisotropic thermal parameters have been deposited as the supplementary data at the Chemical Society of Japan as Document No. 8338.

Results and Discussion

Preparations of Molecular Complexes with TNB. In this study, the 2:1 molecular complexes between TNB and Schiff base copper(II), nickel(II), or palladium (II) complexes with the structure of **1** or **2** have been isolated by mixing a dichloromethane solution of **1** or **2** and an acetone solution of TNB under the reaction conditions noted in the experimental section. Their elemental analytical data are given in Table 2. It seems that the parent complex **1** or **2** forms the molecular complex preferably with TNB rather than with TCNQ, because all the parent complexes which formed the molecular complexes with TCNQ[1] formed the molecular complexes with TNB and some of other **1** or **2** formed the molecular complexes with TNB.

*Crystal and Molecular Structure of Pd(2,1-*i*-C_3H_7)$_2$·2TNB.* Crystal structure projected along the b- and c-axis is presented in Figs. 2 and 3, respectively, showing the overlapping mode and the stacking of Pd (2,1-*i*-C_3H_7)$_2$ and TNB molecules. Bond distances and angles with their estimated standard deviations in parentheses are given in Table 3. Some selected least-squares planes with the deviations of atoms from the plane and the dihedral angles between them are given in Table 4. Donor-acceptor intermolecular distances are given in Table 5.

TABLE 4. EQUATIONS OF LEAST-SQUARES PLANES AND DISTANCES (Å) OF ATOMS FROM THE PLANE (IN BRACKETS)

Plane 1: napthalene ring C(1)-C(10)
$-0.3902x+0.9181y+0.0696z=0.6239$
[O(2) −3.14, O(3) −3.60, O(4) −3.77, O(5) −3.28, O(6) −2.57, O(7) −3.51, C(15) −3.36, C(16) −3.44, C(17) −3.42, C(18) −3.28, C(19) −3.24, C(20) −3.26, Pd −0.62]

Plane 2: TNB O(2)-O(6), N(2)-N(4), C(15)-C(20)
$-0.3549x+0.9255y+0.1518z=-2.2024$
[O(2) 0.22, O(3) −0.06, O(4) −0.19, O(5) 0.14, O(6) 0.46, O(7) −0.49, N(2) 0.08, N(3) −0.02, N(4) −0.04]

Plane 3: Pd, O(1), N(1)
$-0.7362x+0.6760y-0.0318z=0.0000$

Dihedral angle between the planes
Plane 1-Plane 2 5.1° Plane 1-Plane 3 25.1°

As shown in Figs. 2 and 3, the crystal structure consists of π-π type molecular structure in which the donor (naphthalene ring of Pd(2,1-*i*-C_3H_7)$_2$) and the acceptor (TNB) molecules stack alternately. The structure has a center of symmetry and the Pd atom lies at an inversion center. Therefore the Pd atom has a square planar coordination geometry. As shown in Fig. 3, the complex assumes a markedly stepped chair-like shape, where the seat and the rests are formed by the coordination plane (PdO_2N_2) and two 1-(imonomethyl)-2-naphtholato moieties. The Pd atom is deviated by 0.62 Å from the least-squares plane of the naphthalene ring, and the dihedral angle between the coordination plane and the mean plane of the naphthalene ring is 25.1°. The plane of TNB molecule is approximately parallel to the naphthalene ring and the dihedral angle between them is 5.1°. If there was a difference of the molecular structure between the parent palladium(II) and the molecular complex, it should be the degree of the stepped structure, that is, the deviation of Pd atom from the mean plane of the naphthalene moiety, because palladium(II) demands strongly square planar coordination geometry.[9]

The structural feature of the present molecular complex is quite similar to that of Cu(2,1-*i*-C_3H_7)$_2$·2TCNQ,[1] suggesting the generality of the structure with a chair-like shape and the alternately stacking of the donor and acceptor molecules for a series of 2:1 molecular complexes between TCNQ or TNB and **1** or **2**. However, there is a significant difference between Cu(2,1-*i*-C_3H_7)$_2$·2TCNQ and Pd(2,1-*i*-C_3H_7)$_2$·2TNB. When the crystal structure was viewed perpendicular to the donor or acceptor plane, for Cu (2,1-*i*-C_3H_7)$_2$·2TCNQ, the center of TCNQ molecule coincides approximately the center of the naphthalene ring of the complex. On the other hand, for Pd(2,1-*i*-C_3H_7)$_2$·2TNB, the center of TNB molecule coincides approximately the center of terminal benzene ring.

The crystal structure of the 2:1 molecular complex between TNB and bis(*N*-methylsalicylideneaminato)-copper(II) (Cu(Sal-CH_3)$_2$·2TNB) has been determined by the single-crystal X-ray analysis.[10] The crystal structure consists of rather discrete Cu(Sal-CH_3)$_2$·

TABLE 5. DONOR-ACCEPTOR INTERMOLECULAR DISTANCES LESS THAN 3.5 Å OF Pd(2,1-*i*-C_3H_7)$_2$·2TNB

Intermolecular distance		l/Å	Intermolecular distance		l/Å
C(1)-N(4)	1	3.43	C(1)-C(19)	1	3.40
C(1)-C(20)	1	3.50	C(2)-C(20)	1	3.38
C(3)-O(2)	1	3.34	C(4)-C(15)	1	3.44
C(7)-N(3)	1	3.46	C(8)-O(5)	1	3.46
C(9)-C(18)	1	3.34	C(10)-C(18)	1	3.50
C(10)-C(19)	1	3.38	C(11)-O(6)	1	3.14
C(11)-N(4)	1	3.40	C(6)-O(3)	2	3.37
O(5)-C(7)	3	3.40	C(7)-C(15)	2	3.40
C(7)-C(16)	2	3.37	C(9)-C(20)	2	3.47

1: x, y, z; 2: $x, y+1, z$; 3: $1-x, y-1/2, -z+1/2$.

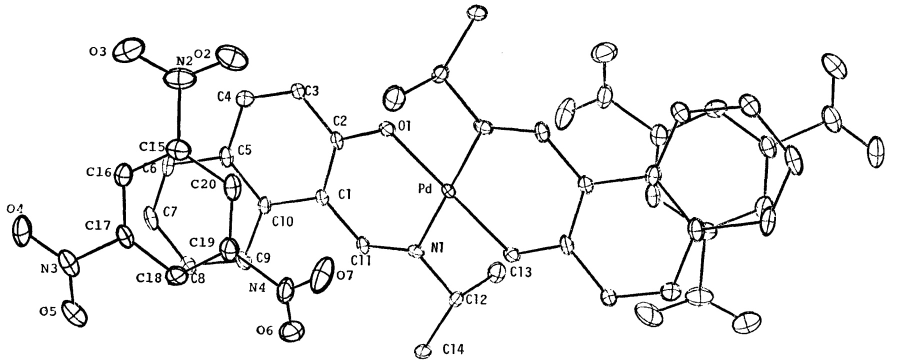

Fig. 2. Crystal structure of $Pd(2,1\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$ projected onto the TNB plane and the atom numbering scheme.

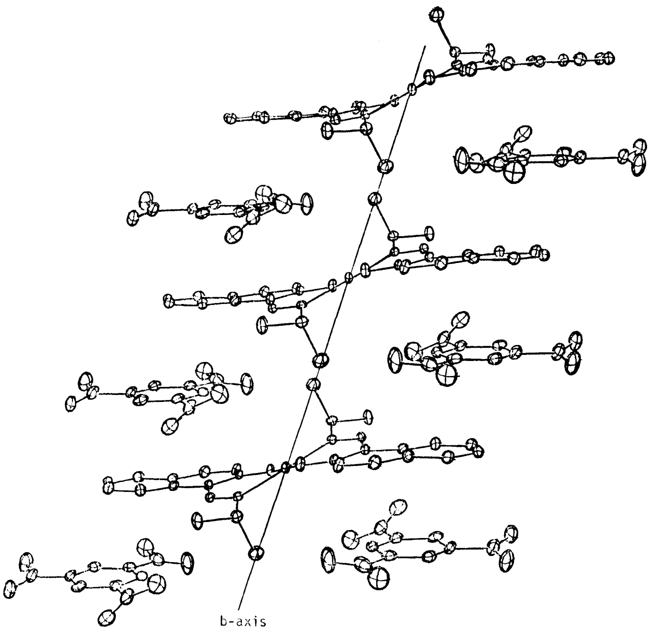

Fig. 3. Crystal structure of $Pd(2,1\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$ projected onto the ab plane.

2TNB unit, because the TNB molecule is approximately parallel to the nearest salicylideneaminato moiety but is tilted to the another neighboring moiety with a tilt angle of 26.4°.

Thermal Analysis. It is well known that some of the bis(*N*-alkylsalicylideneaminato)metal(II) complexes exhibit the isomerization from a square planar form to tetrahedral or polymeric octahedral form in solid state by heating.[11–13] Then the thermal analysis (TGA and DSC) was carried out for the parent complexes $Cu(2,1\text{-}R)_2$ ($R{=}C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_4H_9$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$), $Ni(2,1\text{-}R)_2$ ($R{=}CH_3$, C_2H_5, $n\text{-}C_3H_7$), and $Pd(2,1\text{-}R)_2$ ($R{=}n\text{-}C_4H_9$, $t\text{-}C_4H_9$). Of which $Cu(2,1\text{-}n\text{-}C_4H_9)_2$ and $Ni(2,1\text{-}CH_3)_2$ showed isomerization peak in solid state by heating, as shown in Fig. 4. The DSC curve of $Cu(2,1\text{-}n\text{-}C_4H_9)_2$ posseses two endothermic peaks without weight loss, of which the second peak corresponds to phase transformation from solid to liquid. The endothermic peaks in the solid state can be attributed to the change of the coordination geometry, and the values of 1.80 kcal mol^{-1} for $Cu(2,1\text{-}n\text{-}C_4H_9)_2$ and 1.77 kcal mol^{-1} for $Ni(2,1\text{-}CH_3)_2$ are of the same order of the π-π type donor-acceptor interaction.[14] (1 cal=4.184 J) The palladium(II) complexes showed no isomerization peak, being consistent that palladium(II) strongly demands the square planar geometry.[9] It should be noted that their molecular complexes with TCNQ show no peaks corresponding to the isomerization.[15]

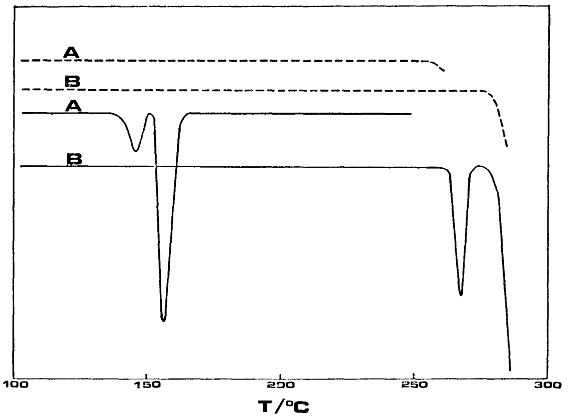

Fig. 4. Thermogravimetric and differential scanning calorimetric curves for $Cu(2,1\text{-}n\text{-}C_4H_9)_2$ (A) and $Ni(2,1\text{-}CH_3)_2$ (B).

Electronic Spectra. Electronic spectra were measured in Nujol mull and in equivolume solution of acetone and chloroform. The solution spectra of the parent complex and its molecular complex with TNB are quite similar to each other in absorption coefficient and band maxima in the region of $(14-22)\times 10^3$ cm^{-1}, in which TNB molecule shows no absorption. On the other hand, in Nujol mull, an intense band appeared at about 18×10^3 cm^{-1}. As a typical example, the electronic spectra of $Ni(2,1\text{-}i\text{-}C_3H_7)_2$ and $Ni(2,1\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$ in Nujol mull and in solution are shown in Fig. 5. Since all the molecular complexes of nickel (II), copper(II), and palladium(II) exhibit this band at about same wave number, this band may be attributable to a charge transfer band between TNB and naphthalene moiety. In the case of the palladium(II) complexes, it is well known that palladium(II) demands strongly square planar configuration[11–13] so that the coordination geometrical change associated with the formation of the molecular complex (at least from

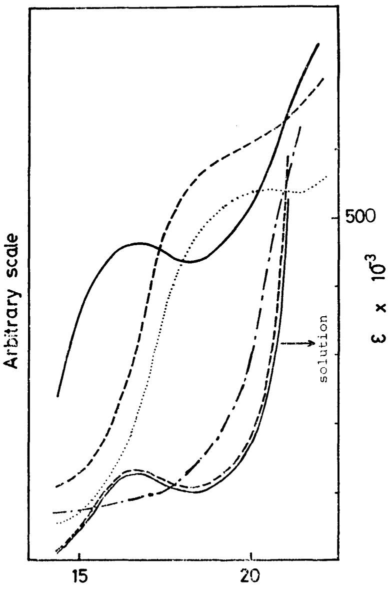

Fig. 5. Electronic spectra of $Ni(2,1\text{-}n\text{-}C_3H_7)_2$ (——) and $Ni(2,1\text{-}n\text{-}C_3H_7)_2\cdot 2TNB$ (— — —) measured in Nujol mull and in a acetone-chloroform solution, and Nujol mull spectra of $Pd(2,1\text{-}i\text{-}C_3H_7)_2$ (—·—) and $Pd(2,1\text{-}i\text{-}C_3H_7)_2\cdot 2TNB$ (······).

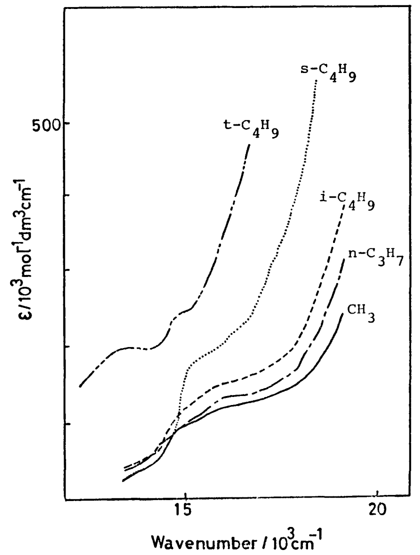

Fig. 6. Electronic spectra of $Cu(2,1\text{-}R)_2$ ($R=CH_3$, $n\text{-}C_3H_7$, $i\text{-}C_4H_9$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$) in chloroform solution.

tetrahedral to square planar) can be deleted. In addition, the electronic spectra of the parent complexes for a series of $Pd(2,1\text{-}R)_2$ ($R=CH_3$, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$) are quite similar to each other and show no absorption band around 18×10^3 cm^{-1}. So this band can be arised from donor-acceptor interaction between TNB and terminal benzene ring. It must be noted that 1:1 molecular complex between naphthalene and TNB (Nap·TNB) did not exhibit the band at the wave number, where the center of Nap coincides the center of TNB so that the overlapping mode[16] is different from that of the present complex. In the case of the copper(II) complexes, the spectra of the parent complexes exhibit d-d transition bands in the region of $(12-18)\times10^3$ cm^{-1} which can provide the information of the coordination geometry, as shown in Fig. 6. Red shift and intensity enchancement of d-d bands are recognized indicators of the transformation from square planar to tetrahedral stereochemistry, as known by the well-established complexes.[17] However, the information with respect to the coordination geometrical change associated with the formation of the molecular complex with TNB is hidden by the intense band at 18×10^3 cm^{-1}.

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