

Four- and Five-Coordinated Nickel(II) Isocyanide Complexes and Donor-Acceptor Complexes Containing Nickel and Mercury^{††}

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Reaction of $\text{NiI}_2(\text{RNC})_2$ (**1**) (**a**: $\text{R}=2,6\text{-Me}_2\text{C}_6\text{H}_3$; **b**: $4\text{-Br-}2,6\text{-Me}_2\text{C}_6\text{H}_2$; **c**: $2,4\text{-}t\text{-Bu}_2\text{-}6\text{-MeC}_6\text{H}_2$; **d**: $2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2$) with RNC or PPh_3 gave $\text{NiI}_2(\text{RNC})_3$ (**2**) or $\text{NiI}_2(\text{PPh}_3)(\text{RNC})_2$ (**3**) (**a**: $\text{R}=2,6\text{-Me}_2\text{C}_6\text{H}_3$; **b**: $2,6\text{-Me}_2\text{-}4\text{-BrC}_6\text{H}_2$). An X-ray analysis of (**3a**) showed that the complex has a trigonal bipyramidal structure; crystal data: Space group $\text{Pna}2_1$; $a=21.577(2)$, $b=9.440(1)$, $c=17.075(1)$ Å, $\alpha=\beta=\gamma=90.0^\circ$, $V=3477.7(6)$ Å³, $R=0.0444$. The bromide and chloride complexes, $\text{NiX}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (**1e**: $\text{X}=\text{Cl}$; **1f**: $\text{X}=\text{Br}$) did not produce five-coordinated species. When complexes (**1a**, **1b**, **1e**, or **1f**) were treated with Hg in the presence of isocyanide, the donor-acceptor complexes $[\text{Ni}(\text{RNC})_4\text{HgX}_2]_2$ ($\text{X}=\text{I}$, Br , or Cl) (**4**) were formed. An X-ray analysis of (**4b**) ($\text{R}=4\text{-Br-}2,6\text{-Me}_2\text{C}_6\text{H}_2$) was undertaken; crystal data: Space group: $\text{P}\bar{1}$ (triclinic); $a=12.709(3)$, $b=16.145(3)$, $c=12.614(3)$ Å, $\alpha=96.11(2)$, $\beta=107.67(2)$, $\gamma=73.11(2)^\circ$, $V=2359.5(10)$ Å³, $R=0.0686$. The complex is a donor-acceptor complex containing the Ni-Hg bond and has a dimeric structure bridged by two I atoms. The configuration around Ni is the trigonal bipyramid and around Hg, distorted tetrahedron.

The low-valent metal complexes often show an instability that is related to the electron-releasing capability of ligands. This instability can be improved by the release of the excess electron density from the metal center. One possible way to reduce the electron density on the metal atom without changing its oxidation state is formation of a donor-acceptor complex. A general preparation of donor-acceptor complexes is arising from interaction of zerovalent complexes with Group 2 metal dihalides.¹⁾ Dixneuf et al have reported that carbene-iron derivatives which were easily oxidized were stabilized by formation of carbene-Fe(O) Hg(II) donor-acceptor complexes on treatment with HgX_2 .²⁾

When $\text{NiX}_2(\text{RNC})_2$ were treated with mercury metal in the presence of isocyanide, an initial electron transfer from Hg^0 to Ni^{2+} occurred, and finally the Ni-Hg donor-acceptor complex was formed. Here we reported preparation and characterization of donor-acceptor complexes and related ones.

Experimental

Isocyanides³⁾ and $\text{NiI}_2(\text{RNC})_2$ ⁴⁾ were prepared by literature methods, some with modification. Electronic and infrared spectra were recorded on Hitachi 330 and JASCO 442 spectrometers, respectively. ¹H NMR spectra were recorded on a JEOL FX100 instrument. Electric conductivities were measured by the Ando Electronic Co. LCR-10 impedance bridge.

Preparation of $\text{trans-NiI}_2(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{NC})_2$ (1d**).** A mixture of NiI_2 (0.57 g, 1 mmol) and $2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2\text{NC}$ (0.12 g, 0.44 mmol) in CH_2Cl_2 (5 ml) was stirred at room temperature. After 1 h, the mixture was filtered and the solvent was removed in vacuo. The residue was crystallized from CH_2Cl_2 -hexane to give the title complex (0.16 g, 86%).

Found: C, 53.45; H, 6.82; N, 3.25%. Calcd for $\text{C}_{38}\text{H}_{58}\text{N}_2\text{I}_2\text{Ni}$: C, 53.36; H, 6.83; N, 3.27%. IR (KBr): 2174 cm^{-1} . ¹H NMR (CDCl_3) $\delta=1.31$ (s, *p-t*-Bu), 1.58 (s, *o-t*-Bu), and 7.33 (s, aromatic protons).

Other nickel(II) complexes were prepared by a similar procedure mentioned above.

$\text{trans-NiI}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (1a**) (88%):** Found: C, 37.59; H, 3.25; N, 4.89%. Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{I}_2\text{Ni}$: C, 37.61; H, 3.16; N, 4.87%. IR (KBr) 2163 cm^{-1} . ¹H NMR (CDCl_3) $\delta=2.52$ (s, Me), and ca. 7.2 (m, aromatic protons). ¹H NMR (a mixture of **1a** and RNC) (CDCl_3) $\delta=2.45$ (s, *o*-Me), and ca. 7.2 (aromatic protons). Electronic spectrum (CH_2Cl_2) λ_{max} 387 (5500 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 342 (3700), 296 (36700), and 237 (23500) nm.

$\text{trans-NiI}_2(2,4\text{-}t\text{-Bu}_2\text{-}6\text{-MeC}_6\text{H}_2\text{NC})_2$ (1c**) (73%):** Found: C, 49.84; H, 6.01; N, 3.63%. Calcd for $\text{C}_{32}\text{H}_{46}\text{N}_2\text{I}_2\text{Ni}$: C, 50.07; H, 6.12; N, 3.67%. IR (nujol) 2168 cm^{-1} . ¹H NMR (CDCl_3) $\delta=1.30$ (s, *p-t*-Bu), 1.50 (s, *m-t*-Bu); 2.49 (s, *m*-Me), and ca. 7.2 (aromatic protons). ¹H NMR (CDCl_3) (a mixture of **1c** and RNC) $\delta=1.30$ (s, *p-t*-Bu), 1.50 (s, *m-t*-Bu), 2.45 (s, *m*-Me), and ca. 7 (aromatic protons). Electronic spectrum (CH_2Cl_2) λ_{max} 453 (1700), 388 (10900), 340 sh (8000), 290 (65700), 262 (40000), and 247.5 (49200) nm.

$\text{trans-NiI}_2(4\text{-Br-}2,6\text{-Me}_2\text{C}_6\text{H}_2\text{NC})_2$ (1b**) (90%):** Found: C, 29.66; H, 2.17; N, 3.73%. Calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{Br}_2\text{I}_2\text{Ni}$: C, 29.51; H, 2.20; N, 3.82%. IR (nujol) 2171 cm^{-1} . Electronic spectrum (CH_2Cl_2) λ_{max} 450 (900), 389 (5900), 346 (4700), 304 (43700), 296 (42800), and 248 (24400) nm.

Preparation of $\text{cis-NiCl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (1e**).** To a solution of $\text{NiCl}_2(\text{PPh}_3)_2$ (0.16 g, 0.25 mmol) in CH_2Cl_2 (10 ml) was added 2,6-xylyl isocyanide (0.075 g, 0.57 mmol) at room temperature. After 1 h, the solution was filtered and the solvent was removed in vacuo. Crystallization of the residue from CH_2Cl_2 and hexane gave orange yellow crystals (0.064 g, 65%). Found: C, 55.05; H, 4.59; N, 7.11%. Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{Cl}_2\text{Ni}$: C, 55.16; H, 4.63; N, 7.15%. IR (nujol) 2208, and 2195 cm^{-1} . ¹H NMR (CDCl_3) $\delta=2.42$ (s, *o*-Me), and ca. 7.0 (aromatic protons). ¹H NMR (CDCl_3) (a mixture of **3a** and RNC) $\delta=2.41$ (s, *o*-Me), and ca. 7 (aromatic protons).

$\text{trans-NiBr}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (1f**),** was prepared from a metathesis of (**1e**) with KBr. Found: C, 44.88; H, 3.89; N, 5.77%. Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{Br}_2\text{Ni}$: C, 44.96; H, 3.77; N, 5.83%.

^{††} Studies on the Interaction of Transition-Metal Complexes 34. For Part 33, see Y. Yamamoto and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, **1989**, 2161.

^1H NMR (CDCl_3) $\delta=2.45$ (s, *o*-Me), ca. 7 (aromatic protons). ^1H NMR (CDCl_3) (**2a** and RNC) $\delta=2.40$ (s, *o*-Me), ca. 7 (aromatic protons). IR (nujol) 2194 cm^{-1} .

Preparation of $\text{NiI}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_3$ (2a**).** 2,6-Xylyl isocyanide (0.07 g, 0.53 mmol) was added to a brown solution of *trans*- $\text{NiI}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (0.20 g, 0.35 mmol) in CH_2Cl_2 (5 ml) at room temperature. The solution color turned blue. Addition of hexane to the solution gave blue crystals (0.21 g, 85.0%) of the title complex. Found: C, 45.63; H, 3.76; N, 5.94%. Calcd for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{I}_2\text{Ni}$: C, 45.93; H, 3.85; N, 5.95%. IR (nujol) 2162 cm^{-1} . ^1H NMR (CDCl_3) $\delta=2.50$ (s, Me), and ca. 7.13 (c, aromatic protons). Electronic spectrum (CH_2Cl_2) λ_{max} 450 sh (680), 386 (5900), 343 (4200), and 295 (37700) nm.

$\text{NiI}_2(4\text{-Br-2,6-Me}_2\text{C}_6\text{H}_2\text{NC})_3$ (**2b**) (75%). Found: C, 34.77; H, 2.43; N, 4.61%. Calcd for $\text{C}_{27}\text{H}_{24}\text{N}_3\text{Br}_3\text{I}_2\text{Ni}$: C, 34.40; H, 2.57; N, 4.46%. IR (nujol) 2160 cm^{-1} .

Preparation of $\text{NiI}_2(\text{PPh}_3)(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2 \cdot 1/3\text{CH}_2\text{Cl}_2$ (3a**).** To an orange solution of *cis*- $\text{NiCl}_2(\text{PPh}_3)_2$ (0.3 g, 0.46 mmol) and 2,6-xylyl isocyanide (0.13 g, 1.0 mmol) in CH_2Cl_2 (10 ml) was added an excess of KI in H_2O (5 ml) at room temperature and the mixture was stirred for 1 h. Organic layer was dried over Na_2SO_4 . Removal of the solvent and crystallization of the residue from CH_2Cl_2 and hexane gave blue crystals (0.26 g, 67.5%). Found: C, 50.25; H, 3.95; N, 3.21%. Calcd for $\text{C}_{36+1/3}\text{H}_{33+(2/3)}\text{N}_2\text{P}_2\text{Cl}_{2/3}\text{I}_2\text{Ni}$: C, 50.42; H, 3.92; N, 3.24%. IR (nujol) 2160 and 2187 cm^{-1} . ^1H NMR (CDCl_3) $\delta=2.20$ (s, Me), 5.29 (s, CH_2), and ca. 7.6 (c, aromatic protons). Electronic spectrum (CH_2Cl_2) λ_{max} 570 (1700), 384 (5100), ca. 340 (7500), and 291 (38000) nm.

4-Bromo-2,6-dimethylphenyl isocyanide complex was also prepared by a similar procedure.

$\text{NiI}_2(\text{PPh}_3)(4\text{-Br-2,6-Me}_2\text{C}_6\text{H}_2\text{NC})_2$ (**3b**) (75%). Found: C, 43.44; H, 3.31; N, 2.84%. Calcd for $\text{C}_{36}\text{H}_{31}\text{N}_2\text{Br}_2\text{I}_2\text{Ni}$: C, 43.46; H, 3.14; N, 2.82%. IR (nujol) 2160 cm^{-1} .

Preparation of $[\text{Ni}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4][\text{PF}_6] \cdot \text{CH}_2\text{Cl}_2$. When $[\text{NH}_4][\text{PF}_6]$ was added to a brown solution of NiBr_2 (0.32 g, 1.47 mmol) and 2,6-xylyl isocyanide (0.393 g, 3.0 mmol) in THF (15 ml), the solution turned wine red. After the mixture was heated at 60°C for 2 h, the solvent was removed in vacuo and the residue was extracted with CH_2Cl_2 . The solvent was removed to ca. 5 ml and hexane was added, giving brown crystals (0.38 g, 53%) containing one molecule of CH_2Cl_2 as a solvated molecule. Found: C, 46.87; H, 4.02; N, 5.93%. Calcd for $\text{C}_{37}\text{H}_{38}\text{N}_4\text{P}_2\text{F}_{12}\text{Cl}_2\text{Ni}$: C, 46.38; H, 4.00; N, 5.85%. IR (nujol) 2176 and 2192 cm^{-1} . ^1H NMR (CDCl_3) $\delta=2.53$ (s, Me), 5.30 (s, CH_2), and ca. 7.1 (aromatic protons).

Preparation of $[\text{Ni}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4\text{HgI}_2]_2$ (4a**).** (a) Reaction of *trans*- $\text{NiI}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ with mercury in the presence of 2,6-xylyl isocyanide. A mixture of *trans*- $\text{NiI}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (0.11 g, 0.19 mmol), 2,6-xylyl isocyanide (0.03 g, 0.23 mmol) and Hg (ca. 2 ml) in CH_3CN (10 ml) was stirred for 2.5 h at room temperature, forming the dark yellow precipitate. The organic layer was dried and the residue was extracted with benzene. The solvent was dried to ca. 3 ml and hexane was added, giving brown crystals (0.14 g, 71%) of the title complex. Found: C, 41.58; H, 3.44; N, 5.27%. Calcd for $\text{C}_{72}\text{H}_{72}\text{N}_8\text{I}_4\text{Hg}_2\text{Ni}_2$: C, 41.66; H, 3.50; N, 5.40%. IR (nujol) 2139 and 2081 cm^{-1} . ^1H NMR (CDCl_3) $\delta=2.50$ (s, Me), ca. 7 (aromatic protons). Electronic spectrum (CH_2Cl_2) λ_{max} ca. 360 sh (10400), 305 (20700), 237 sh (27700), and 231 (29400) nm.

(b) Reaction of $\text{Ni}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4$ with HgI_2 . 2,6-Xylyl isocyanide. To a suspension of $\text{Ni}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4$ (0.26 g,

0.45 mmol) in CH_3CN (15 ml) was added HgI_2 (0.2 g, 0.44 mmol). After stirring for 5 h at room temperature, the mixture was filtered and the solvent was removed in vacuo. Recrystallization of the residue from CH_2Cl_2 –hexane gave brown crystals.

The following complexes were prepared by the procedure (a).

4-Bromo-2,6-dimethyl isocyanide complex, $[\text{Ni}(4\text{-Br-2,6-Me}_2\text{C}_6\text{H}_3\text{NC})_4\text{HgI}_2]_2$ (**4b**) (87%), was also prepared from the reaction of *trans*- $\text{NiI}_2(4\text{-Br-2,6-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ with mercury in the presence of 4-bromo-2,6-dimethylphenyl isocyanide. Found: C, 35.15; H, 2.69; N, 3.91%. Calcd for $\text{C}_{84}\text{H}_{76}\text{N}_8\text{Br}_4\text{I}_4\text{Hg}_2\text{Ni}_2$: C, 35.24; H, 2.68; N, 3.91%. IR (nujol) 2141 and 2082 cm^{-1} . ^1H NMR (CDCl_3) $\delta=1.55$ (s, 6H, Me), 2.44 (s, 18H, Me), and 7.37 (benzene and aromatic protons). Electronic spectrum (CH_2Cl_2) λ_{max} ca. 360 sh (11300) and 313 (20300) nm.

$[\text{Ni}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4\text{HgCl}_2]_2$ (**4c**) (65%). Found: C, 50.05; H, 4.21; N, 6.47%. Calcd for $\text{C}_{36}\text{H}_{36}\text{N}_4\text{Cl}_2\text{HgNi}$: C, 50.58; H, 4.24; N, 6.55%. IR (nujol) 2165 and 2104 cm^{-1} . ^1H NMR (CDCl_3) $\delta=2.49$ (s, Me), and ca. 7.0 (aromatic protons). Electronic spectrum (CH_2Cl_2): λ_{max} 330 sh (9500) and 280 (15000) nm.

$[\text{Ni}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4\text{HgBr}_2]_2$ (**4f**) (68%). Found: C, 45.83; H, 3.85; N, 5.76%. Calcd for $\text{C}_{36}\text{H}_{36}\text{N}_4\text{Br}_2\text{HgNi}$: C, 45.80; H, 3.84; N, 5.94%. IR (nujol) 2165 and 2101 cm^{-1} . ^1H NMR (CDCl_3) $\delta=2.58$ (s, Me), ca. 7.0 (aromatic protons). Electronic spectrum (CH_2Cl_2) λ_{max} 312 sh (19000).

Preparation of $[\text{Ni}(\text{PPh}_3)(4\text{-Br-2,6-Me}_2\text{C}_6\text{H}_2\text{NC})_3\text{HgI}_2]_2$ (5b**).** Mercury was added to a blue solution of $\text{NiI}_2(\text{PPh}_3)(4\text{-Br-2,6-Me}_2\text{C}_6\text{H}_3\text{NC})_2$ (0.14 g, 0.14 mmol) and 4-bromo-2,6-dimethylphenyl isocyanide (0.03 g, 0.14 mmol) in benzene (10 ml) and the mixture was stirred for 0.5 h at room temperature, changing an orange solution. The mixture was filtered and the solvent was removed to ca. 3 ml. Hexane was added, giving orange crystals (0.134 g, 68%) of the title complex. Found: C, 38.51; H, 2.77; N, 3.01%. Calcd for $\text{C}_{90}\text{H}_{78}\text{N}_6\text{Br}_6\text{I}_4\text{P}_2\text{Hg}_2\text{Ni}_2$: C, 38.45; H, 2.80; N, 2.99%. IR (nujol) 2075 and 2085 cm^{-1} . ^1H NMR (CDCl_3) $\delta=2.14$ (s, Me), and ca. 7.3 (aromatic protons). Electronic spectrum (CH_2Cl_2) λ_{max} 396 (15500), 323 (27400), and 260 sh (37800) nm.

$[\text{Ni}(\text{PPh}_3)(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_3\text{HgI}_2]_2(\text{CH}_2\text{Cl}_2)_3$ (**5a**) was recrystallized from CH_2Cl_2 and hexane. Found: C, 43.33; H, 3.44; N, 3.14%. Calcd for $\text{C}_{93}\text{H}_{90}\text{N}_6\text{Cl}_6\text{P}_2\text{I}_4\text{Hg}_2\text{Ni}_2$: C, 43.08; H, 3.50; N, 3.24%. IR (nujol) 2082 cm^{-1} . ^1H NMR (CDCl_3) $\delta=2.23$ (s, Me), 5.29 (s, CH_2), and ca. 7.3 (aromatic protons). Electronic spectrum (CH_2Cl_2) λ_{max} 394 (10000), 314 (18600), and 260 (46800) nm.

Data Collection and Solution of the Structure. Complex (**3a**) was recrystallized from CH_2Cl_2 –benzene, and **4b**, from benzene–hexane, respectively. Weissenberg photographs indicated that the crystals of **3a** were orthorhombic with space group $Pna2_1$ and those of **4b**, triclinic with the space group $P\bar{1}$. Cell constants of **3a** were determined from 18 reflections ($11^\circ < 2\theta < 22^\circ$), and those of **4b** from 20 reflections ($12^\circ < 2\theta < 25^\circ$) on a Rigaku automated diffractometer. Details of the crystal parameters along with data collection are summarized in Table 1. Intensities were corrected for Lorentz and polarization effects. No absorption corrections were made; the absorption coefficient of **4b** is large, but the crystal used for data collection was not well-shaped one to make correction. The positions of the heavy atoms were determined by a Patterson map using the UNICS III program system.⁵⁾

The remaining atoms were located in succeeding different Fourier syntheses. The positions of all atoms for **3a**, and of Hg, Ni, and Br atoms for **4b** were refined anisotropically by using block-diagonal least-squares methods. Final difference

Fourier maps of **3a** and **4b** showed smaller residual peaks than $0.6 \text{ e } \text{\AA}^{-3}$. No attempts were made to locate the hydrogen atoms. The positional parameters are given in Tables 2 and 3. Anomalous dispersion effects and atomic scattering factors

Table 1. Crystal Data and Experimental Details

Compd	3a	4b^{a)}
Formula	$\text{C}_{36}\text{H}_{33}\text{N}_2\text{PI}_2\text{Ni}$	$\text{C}_{84}\text{H}_{76}\text{N}_8\text{Br}_8\text{I}_4\text{Hg}_2\text{Ni}_2$
F. W.	837.2	2363.1
Crystal system	Orthorhombic	Triclinic
Space group	$Pna2_1$	$P\bar{1}$
$a/\text{\AA}$	21.577(2)	12.709(3)
$b/\text{\AA}$	9.440(1)	16.145(3)
$c/\text{\AA}$	17.075(1)	12.614(3)
α/deg	90.0	96.11(2)
β/deg	90.0	107.67(2)
γ/deg	90.0	73.11(2)
$V/\text{\AA}^3$	3477.7(6)	2359.5(10)
Z	4	2
Crystal size/mm	$0.2 \times 0.17 \times 0.30$	— ^{b)}
$D_x/\text{g cm}^{-3}$	1.60	2.01
$\mu (\text{Mo K}\alpha)/\text{cm}^{-1}$	23.9	83.3
Radiatn	MoK α ($\lambda=0.71073 \text{ \AA}$ from graphite monochromator)	
Scan speed/deg	4 in $2\theta \text{ min}^{-1}$	4 in $2\theta \text{ min}^{-1}$
2θ limits/deg	3.0–45.0	3.0–50.0
Scan mode	ω scan for $2\theta \leq 30$	ω – 2θ scan for $2\theta > 30$
Unique data measd	2739	4789
Unique data used ($F_o > 3\sigma(F_o)$)	2639	4555
No. of variables	380	258
$F(000)$	1648	1344
R^c	0.0444	0.0686
R_w^d	0.0457	0.0728

a) Measurement was carried out in a capillary. Benzene is contained as a solvated molecule. b) The well-shaped crystal to measure the crystal size was not obtained. c) $R = \sum \|F_o| - |F_c| \| / \sum |F_o|$. d) $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

Table 2. Atomic Parameters of $[\text{NiI}_2(\text{PPh}_3)(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2]$ (**3a**)^{a)}

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Ni	3474(1)	302(2)	627(1)	3.1(0.0)	C(26)	344(1)	−328(2)	−166(1)	5.0(0.4)
I(1)	2783(0)	2321(1)	0(0)	4.6(0.0)	C(27)	339(1)	66(2)	−223(1)	5.6(0.5)
I(2)	2773(0)	−1735(1)	1213(1)	4.9(0.0)	C(28)	351(1)	−412(2)	−92(1)	7.2(0.7)
P	4507(1)	404(4)	807(2)	3.1(0.1)	C(31)	489(1)	150(1)	8(1)	3.4(0.3)
N(10)	330(1)	170(1)	218(1)	4.0(0.3)	C(32)	556(1)	178(2)	13(1)	5.4(0.5)
C(10)	335(1)	117(1)	159(1)	3.2(0.3)	C(33)	582(1)	266(2)	−43(1)	5.7(0.5)
C(11)	325(1)	243(2)	290(1)	3.9(0.4)	C(34)	547(1)	322(2)	−106(1)	6.1(0.5)
C(12)	318(1)	159(2)	355(1)	4.7(0.4)	C(35)	485(1)	294(2)	−111(1)	5.2(0.5)
C(13)	312(1)	229(2)	427(1)	5.9(0.5)	C(36)	456(1)	209(2)	−54(1)	4.1(0.4)
C(14)	310(1)	380(2)	429(1)	6.0(0.5)	C(41)	474(1)	114(2)	174(1)	3.7(0.4)
C(15)	317(1)	462(2)	361(1)	5.1(0.5)	C(42)	484(1)	261(2)	183(1)	4.6(0.4)
C(16)	324(1)	394(2)	288(1)	3.5(0.3)	C(43)	495(1)	319(2)	258(1)	6.0(0.5)
C(17)	315(1)	−0.5(0.2)	352(1)	6.0(0.5)	C(44)	494(1)	230(2)	323(1)	6.1(0.6)
C(18)	333(1)	472(2)	213(1)	5.7(0.5)	C(45)	486(1)	88(2)	314(1)	6.2(0.6)
N(20)	350(0)	−112(1)	−91(1)	3.4(0.3)	C(46)	474(1)	25(2)	241(1)	5.0(0.4)
C(20)	351(1)	−58(2)	−31(1)	3.5(0.3)	C(51)	489(1)	−132(1)	78(1)	4.1(0.4)
C(21)	344(1)	−180(2)	−166(1)	4.7(0.4)	C(52)	552(1)	−147(2)	97(1)	5.9(0.5)
C(22)	338(1)	−86(2)	−231(1)	4.8(0.4)	C(53)	580(1)	−278(2)	95(1)	7.2(0.6)
C(23)	328(1)	−160(2)	−305(1)	6.9(0.6)	C(54)	548(1)	−396(2)	80(1)	7.0(0.6)
C(24)	329(1)	−310(2)	−305(1)	6.6(0.6)	C(55)	486(1)	−391(2)	62(1)	6.8(0.6)
C(25)	335(1)	−397(2)	−241(1)	6.2(0.6)	C(56)	455(1)	−254(2)	64(1)	5.7(0.5)

a) Positional parameters are multiplied by 10^3 except atoms from Ni to P. The equivalent temperature factors, $B_{\text{eq}} = (4/3) \sum \sum \beta_{ij}(a_i a_j)$ are multiplied by 10^2 .

Table 3. Atomic Parameters of $[\text{Ni}(\text{4-Br-2,6-Me}_2\text{C}_6\text{H}_2\text{NC})_4\text{HgI}]_2$ (**4b**)^{a)}

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Hg	-427(1)	1175(1)	4306(1)	4.9(0.0)	C28	405(2)	122(2)	566(2)	7.2(0.6)
Ni	53(2)	2492(1)	5565(2)	3.8(0.1)	C30	52(2)	171(1)	674(2)	4.8(0.4)
I1	-1306(1)	1449(1)	2069(1)	5.7(0.1)	N30	88(1)	138(1)	758(1)	5.1(0.4)
I2	1642(1)	-314(1)	4758(1)	5.1(0.0)	C31	139(2)	101(1)	864(2)	5.2(0.4)
Br10	-7578(2)	4599(2)	4152(4)	13.2(0.2)	C32	65(2)	98(1)	928(2)	4.6(0.4)
Br20	5845(3)	1651(2)	2526(3)	9.5(0.1)	C33	113(2)	64(1)	1033(2)	5.4(0.5)
Br30	3000(3)	-99(2)	12160(2)	9.3(0.1)	C34	232(2)	35(1)	1033(2)	5.4(0.5)
Br40	2184(8)	6163(3)	11011(5)	28.5(0.5)	C35	305(2)	37(1)	1008(2)	6.0(0.5)
C10	-151(2)	286(1)	501(2)	5.0(0.4)	C36	256(2)	70(1)	902(2)	5.3(0.5)
N10	-253(1)	315(1)	478(1)	5.4(0.4)	C37	-65(2)	131(2)	879(2)	7.1(0.6)
C11	-374(2)	350(1)	462(2)	5.4(0.5)	C38	328(3)	72(2)	824(3)	9.1(0.8)
C12	-434(2)	395(2)	369(2)	6.4(0.5)	C40	35(2)	345(1)	642(2)	4.3(0.4)
C13	-558(2)	431(2)	353(2)	7.1(0.6)	N40	59(1)	400(1)	703(1)	5.0(0.3)
C14	-590(2)	412(2)	439(2)	7.9(0.7)	C41	93(2)	453(1)	792(2)	5.5(0.5)
C15	-536(2)	364(2)	531(2)	8.2(0.7)	C42	104(2)	535(1)	776(2)	5.4(0.5)
C16	-410(2)	330(2)	546(2)	6.9(0.6)	C43	144(2)	585(2)	866(2)	8.3(0.7)
C17	-385(3)	415(2)	285(3)	9.5(0.8)	C44	164(3)	557(2)	965(3)	11.5(1.0)
C18	-341(2)	274(2)	643(2)	8.5(0.7)	C45	148(4)	477(3)	994(4)	14.8(1.3)
C20	110(2)	227(1)	477(2)	4.1(0.4)	C46	123(3)	421(2)	898(3)	11.2(1.0)
N20	183(1)	213(1)	433(1)	4.8(0.3)	C47	77(2)	563(1)	661(2)	6.1(0.5)
C21	278(2)	199(1)	385(2)	4.3(0.4)	C48	102(4)	329(3)	914(4)	15.7(1.5)
C22	253(2)	228(1)	283(2)	4.7(0.4)	C1	-597(4)	309(3)	-197(4)	14.7(1.3)
C23	348(2)	216(2)	239(2)	6.6(0.5)	C2	-503(4)	234(3)	-149(4)	14.3(1.3)
C24	456(2)	175(1)	310(2)	6.0(0.5)	C3	-429(4)	230(3)	-50(4)	15.6(1.5)
C25	478(2)	147(1)	409(2)	6.1(0.5)	C4	-432(7)	295(5)	5(7)	28.2(3.1)
C26	387(2)	154(1)	454(2)	5.5(0.5)	C5	-513(6)	382(5)	-36(6)	27.5(3.0)
C27	131(2)	270(2)	210(2)	7.3(0.6)	C6	-592(4)	381(3)	134(4)	14.5(1.3)

a) Positional parameters are multiplied by 10^4 (from Hg to Br40) and by 10^3 (from C10 to C6). The atoms from Hg to Br40 were anisotropically defined and other atoms were isotropically defined. The equivalent temperature factors, $B_{\text{eq}} = (4/3) \sum \sum \beta_{ij} (a_i a_j)$ are multiplied by 10^2 .

were taken from the usual tabulation.⁶⁾

Results and Discussion

Preparation of *trans*- and *cis*-NiX₂(RNC)₂ and Related Complexes. Orange or brown complexes, NiI₂(RNC)₂ (**1a**: R=2,6-Me₂C₆H₃; **1b**: R=4-Br-2,6-Me₂C₆H₂; **1c**: R=2,4-*t*-Bu₂-6-MeC₆H₂; **1d**: 2,4,6-*t*-Bu₃C₆H₂) were prepared from reactions of NiI₂ with isocyanides, according to literature methods.⁴⁾ The chloride complex, NiCl₂(RNC)₂ (R=2,6-Me₂C₆H₃) (**1e**) was prepared by a substitution reaction of dichlorobis(triphenylphosphine)nickel(II) with isocyanide. The bromide, NiBr₂(RNC)₂ (R=2,6-Me₂C₆H₃) (**1f**) was obtained by a metathesis of the chloride complex with KBr. The infrared spectra showed only one sharp band at ca. 2100 cm⁻¹ ($\nu(\text{N}\equiv\text{C})$) for iodide and bromide complexes, and two peaks for the chloride one. The iodide and bromide complexes have a *trans*-configuration and the latter, a *cis*-one.

The reaction of **1a** or **1b** with an appropriate isocyanide or PPh₃ gave blue complexes formulated as NiI₂(RNC)₃ (**2a**: R=2,6-Me₂C₆H₃; **2b**: R=4-Br-2,6-Me₂C₆H₂) and NiI₂(PPh₃)(RNC)₂ (**3a**: R=2,6-Me₂C₆H₃, **3b**: R=4-Br-2,6-Me₂C₆H₂), respectively. It was supported by an X-ray analysis of **3a** that complexes **2** and **3** have the trigonal bipyramidal structure (Fig. 1).

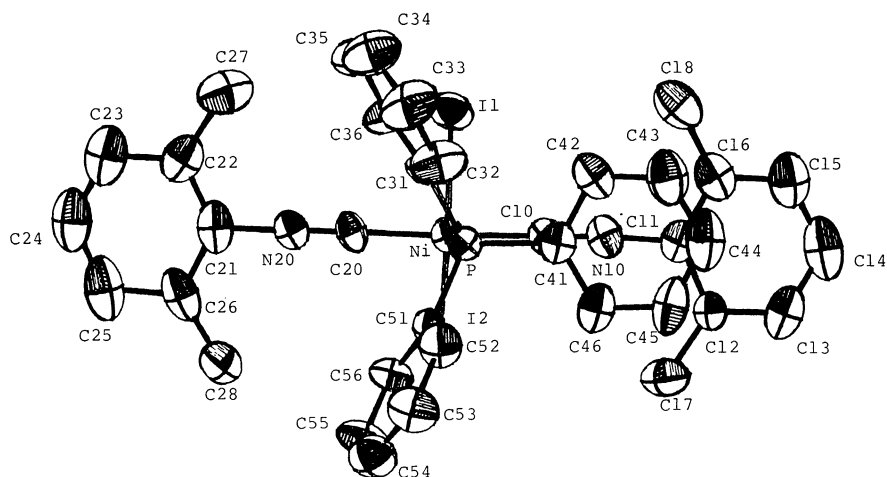
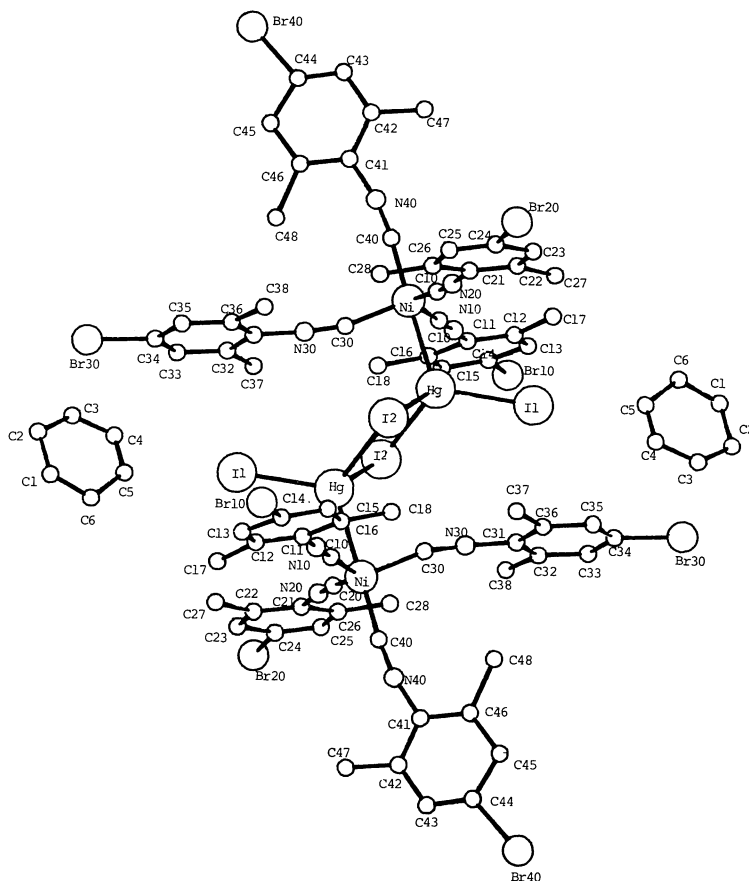
The basal plane has been occupied by two I's and a

phosphine, and two isocyanide ligands have been in the apical positions. The ¹H NMR spectrum of **2a** showed only one singlet at $\delta=2.50$ for *o*-methyl protons, suggesting an intramolecular exchange between apical and basal isocyanide ligands. In the ¹H NMR spectrum of a mixture of **2a** and 2,6-xylyl isocyanide only one singlet due to *o*-methyl groups appeared at $\delta=2.45$, and the electric conductivity of the mixture showed to be a nonelectrolyte. This behavior is due to an inter- and intramolecular ligand exchange.

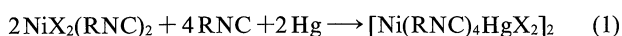
Brown solution of **1f** changed blue reminiscent of a five-coordinated species, when 2,6-xylyl isocyanide was added to **1f** in CH₂Cl₂. Some attempts to isolate a blue species were unsuccessful with recovery of **1f**. A similar reaction was carried out for the chloride complex **1e**. Color change has not been observed and the electronic spectrum of the mixture is similar to that of **1e**, showing that a five-coordinate species does not exist. Five-coordinated species with I are more stable than those with Br and Cl, probably due to higher coordination ability than the other halogens.

In the reaction of **1c** or **1d** containing bulky isocyanide, no assignment responsible for the formation of five-coordinated species was observed, and the starting complex was recovered, due to steric bulkiness.

Donor-Acceptor Complexes. When mercury was added to a solution of **1b** in CH₃CN, brown crystals

Fig. 1. Molecular structure of $[\text{NiI}_2(\text{PPh}_3)(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2]$ (**3a**).Fig. 2. Molecular structure of $[\text{Ni}(4\text{-Br-2,6-Me}_2\text{C}_6\text{H}_2\text{NC})_4\text{HgI}_2]$ (**4b**).

formulated as $[\text{Ni}(4\text{-Br-2,6-Me}_2\text{C}_6\text{H}_2\text{NC})_4\text{HgI}_2]$ (**4b**) were obtained. A similar reaction



occurred in the presence of 4-bromo-2,6-dimethylphenyl isocyanide to give **4b** quantitatively. The structure was determined by an X-ray analysis (Fig. 2).

The spectroscopic studies of **4b** were in good agreement with the crystal structure. The infrared spectrum showed two $\nu(\text{N}\equiv\text{C})$ peaks at $2050\text{--}2150\text{ cm}^{-1}$, being in higher energy region than those of the parent zerovalent complexes and in lower energy than those of divalent complexes, suggesting partial charge transfer from nickel to mercury. Similar infrared behaviors have been noted in the molybdenum–mercury bonded

complexes.⁷⁾

The ¹H NMR spectrum showed two characteristic peaks at $\delta=1.55$ and 2.44 consisting of a 1:3 intensity ratio, assigned to the apical and basal isocyanide ligands, respectively. The ¹H NMR spectrum of a mixture of **4b** and 4-bromo-2,6-dimethylphenyl isocyanide showed two singlets at $\delta=1.56$ and 2.44 for *o*-methyl protons. The former intensity increased with added isocyanide, showing that ligand exchange between the apical and free isocyanide ligands has occurred. The ligand in a trans position to a Ni-Hg bond is more labile than the basal ones. It has been known that isocyanide ligands in a trans position to M-M bond were preferentially replaced by PPh₃ in the reactions of [L₃M-ML₃]²⁺ (M=Pd, Pt; L=RNC) with triphenylphosphine.⁸⁾ Similar donor-acceptor complexes [Ni(2,6-Me₂C₆H₃NC)₄HgX₂]₂ (**4a**: X=I; **4e**: X=Cl; **4f**: X=Br) were prepared from **1a**, **1e**, or **1f** with mercury in the presence of 2,6-xylyl isocyanide. The ¹H NMR spectra of these complexes showed only one singlet at ca. $\delta=2.50$ for *o*-methyl protons, suggesting an intermolecular ligand exchange. 2,6-Xylyl isocyanide ligand is more labile than 4-bromo-2,6-dimethylphenyl isocyanide, related with an electron-acceptor ability. These donor-acceptor complexes were also obtained by the usual treatment of Ni(RNC)₄ with HgI₂.

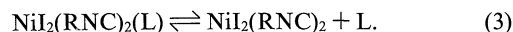


The phosphine complexes, [Ni(PPh₃)(RNC)₃HgI₂]₂ (**5a**: R=2,6-Me₂C₆H₃; **5b** R=4-Br-2,6-Me₂C₆H₂) were prepared by the reaction of NiI₂(PPh₃)(RNC)₂ with mercury in the presence of isocyanide. The infrared spectrum showed two N≡C stretching frequencies at 2070 and 2090 cm⁻¹, in lower energy region than those of the parent complex, due to greater σ -donor ability of triphenylphosphine than isocyanide. The ¹H NMR spectrum showed a singlet at $\delta=\text{ca. } 2.17$ for *o*-methyl protons. We tentatively assumed that the apical isocyanide was replaced by triphenylphosphine, because of labile property of the apical ligand as shown in the ¹H NMR spectrum of **4b**.

Rossi and Hoffmann have concluded from a molecular orbital treatment of five-coordinated d⁸ complexes that good σ -donor ligands will prefer axial site, while good π -acceptor will prefer the equatorial sites.⁹⁾ The configuration of these complexes is in agreement with the proposal.

Electronic Spectra. The electronic spectrum of a 1.25×10^{-4} M (M=mol dm⁻³) solution of **3a** in CH₂Cl₂ showed two peaks at 569 and 367 nm, and two shoulder peaks at ca. 455 and 340 nm. With decrease of the solution concentration (2.51×10^{-5} M), the peak at 569 nm disappeared and the shoulder at ca. 340 nm decreased. Finally the spectrum consisted with that of **1a**, suggesting that triphenylphosphine in the basal plane is more labile than isocyanide ligands in the apical plane.

Similar spectroscopic changes have been observed in **2a**. When RNC or PPh₃ (ca. 20 times per the complex) was added to a ca. 10^{-5} M solution of NiI₂(RNC)₂ or NiI₂(RNC)₃ in CH₂Cl₂, a new peak appeared at ca. 570 nm. The similar behavior was observed in a mixture of **1f** and 2,6-xylyl isocyanide (1: ca. 100 ratio), but the complex (**1e**) did not showed formation of a five-coordinated species even in the presence of a large excess of 2,6-xylyl isocyanide. These results showed the presence of the following equilibrium (trigonal bipyramidal $\rightleftharpoons$ square planar), where L is RNC or PPh₃.



The equilibrium of **2** or **3** lies far to the left in a high concentration or in the presence of an appropriate ligand. The electronic spectrum of **4** showed two peaks at ca. 250 and 310 nm, shifted to shorter wavelength than that of the parent zerovalent complex, probably accompanied with Ni $\rightarrow\pi^*(\text{CNR})$. The λ_{max} values of **4** red-shifted with Cl, Br, and I. Bathochromic shift was observed in the triphenylphosphine derivative **5**. These are related with the electron acceptor ability.

Structures of NiI₂(PPh₃)(2,6-Me₂C₆H₃NC)₂ (3a**) and [Ni(4-Br-2,6-Me₂C₆H₂NC)₄HgI₂]₂ (**4b**).** **Structure of 3a.** The blue complex (**3a**) has a distorted trigonal bipyramidal structure, in which two isocyanide ligands occupied apical positions, and two I atoms and a phosphine, a basal plane. This structure is in disagreement with Rossi and Hoffmann's result.⁹⁾ The average bond angle of I-Ni-P is 124°, wider than a theoretical angle and the I-Ni-I angle is 110°, narrower than an ideal angle. The bond angle of C(10)-Ni-C(20) is 174°, bent away from triphenylphosphine. These are responsible for steric influence of bulky phosphine. The average Ni-I bond is 2.645 Å, comparable with usual Ni-I bond distance. The Ni-C(10) bond length of 1.85(1) Å is longer than 1.81(1) Å of the Ni-C(20) bond. Phenyl rings of apical isocyanide ligands are almost parallel to one phenyl ring of triphenylphosphine (C41-C46) [172.4(6) and 164.1(6)°]. These likely minimized steric interaction between aromatic rings of isocyanide and triphenylphosphine. Dihedral angles between the NiI₂P plane and phenyl rings of apical ligands (C11-C16 and C21-C26) are 92.1(4) and 78.4(5)°, respectively, again due to releasing of steric interaction.

Structure of 4b. The geometry around nickel atom is a distorted trigonal bipyramid. The Hg-Ni-C(40) bond is linear. The nickel atom is occupied upward by 0.33 Å from the triangular C(10)C(20)C(30) plane (a mean angle of C(40)-Ni-C: 100.0°), and the average C-Ni-C angle associated with the triangle C(10)C(20)C(30) are ca. 117°. The plane [C(10)C(20)C(30)] is almost parallel to phenyl rings of isocyanide ligands in the apical sites, minimizing repulsive interaction with axial ligands. The geometry around mercury atom was essentially tetrahedral with the main distortion. The Ni-Hg-I and

I–Hg–I bond angles except the I(2)–Hg–I(2') bond angle of 92.1(5)° containing a bridged ligands, is in the range 108.8–116.6°. The bond length of Hg–Ni is 2.619(3) Å, being comparable with the sum (2.59 Å) of the covalent radii. The Hg–I (bridged) distances (2.954(1) and 2.900(2) Å) are longer than that of Hg–I (terminal) bond (2.734(2) Å). They were shorter than the terminal and bridged Hg–I distances (2.681(1) (terminal) and 2.982(1) and 2.937(1) (bridged) in [(Ph₃PC₅H₄)Hg(μ-I)I]₂.¹⁰ The C–N triple bond length are usual. The Ni–C–N and C–N–C bond angles are similar to those found in usual isocyanide complexes. The Hg–I(2)–Hg bond angle is 87.9°, comparable with that in [(Ph₃PC₅H₄)Hg(μ-I)I]₂.¹⁰

Supplemental Materials.

Thermal parameters (Tables 1 and 3), bond distances

Table 4. Selected Bond Distances and Angles of **3a**

Bond distance (Å)			
Ni–I(1)	2.646(2)	Ni–I(2)	2.644(2)
Ni–P	2.252(3)	Ni–C(10)	1.849(13)
Ni–C(20)	1.806(13)	C(10)–C(20)	1.135(17)
C(20)–N(20)	1.142(16)	N(10)–C(11)	1.414(19)
N(20)–C(21)	1.440(18)		
Bond angle (deg)			
I(1)–Ni–I(2)	110.71(6)	I(1)–Ni–C(10)	87.57(39)
I(1)–Ni–C(20)	90.01(43)	I(1)–Ni–P	125.63(12)
I(2)–Ni–C(10)	84.49(39)	I(2)–Ni–C(20)	91.53(43)
I(2)–Ni–P	123.11(12)	C(10)–Ni–C(20)	174.29(53)
C(10)–Ni–P	90.21(37)	C(20)–Ni–P	95.40(40)
Ni–C(10)–N(10)	177.0(11)	C(10)–N(10)–C(21)	177.3(14)
Ni–C(20)–N(20)	176.2(11)	C(20)–N(20)–C(21)	175.4(12)

and angles (Tables 2 and 4), and Tables of $F_o - F_c$ are available. The tables of thermal parameters, all the bond distances and angles, and observed and calculated structural factors are deposited as Document No. 8969 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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Table 5. Selected Bond Distances and Angles of **4b**

Bond distance (Å)			
Hg–Ni	2.619(3)	Hg–I(1)	2.734(2)
Hg–I(2)	2.954(1)	Hg–I(2')	2.900(2)
Ni–C(10)	1.836(19)	Ni–C(20)	1.837(22)
Ni–C(30)	1.884(21)	Ni–C(40)	1.853(19)
C(10)–N(10)	1.195(26)	N(10)–C(11)	1.428(28)
C(20)–N(20)	1.174(29)	N(20)–C(21)	1.460(30)
C(30)–N(30)	1.145(26)	N(30)–C(31)	1.409(26)
C(40)–N(40)	1.164(25)	N(40)–C(41)	1.364(26)
Bond angle (deg)			
Ni–Hg–I(1)	116.62(7)	Ni–Hg–I(2)	108.84(6)
Ni–Hg–I(2')	111.1(6)	I(1)–Hg–I(2)	110.24(5)
I(1)–Hg–I(2')	115.1(3)	I(2)–Hg–I(2')	92.1(5)
Hg–Ni–C(10)	77.5(6)	Hg–Ni–C(20)	78.5(6)
Hg–Ni–C(30)	84.3(6)	Hg–Ni–C(40)	178.0(5)
C(10)–Ni–C(20)	126.7(9)	C(10)–Hg–C(30)	84.3(6)
Hg–Ni–C(40)	178.0(5)	C(10)–Ni–C(20)	126.7(9)
C(10)–Ni–C(30)	112.3(10)	C(10)–Ni–C(40)	100.8(8)
C(20)–Ni–C(30)	111.7(8)	C(20)–Ni–C(40)	101.9(10)
C(30)–Ni–C(40)	97.4(9)	Ni–C(10)–N(10)	171.0(18)
Ni–C(20)–N(20)	175.3(15)	Ni–C(30)–N(30)	166.1(19)
Ni–C(40)–N(40)	173.9(16)	C(10)–N(10)–C(11)	175.0(22)
C(20)–N(20)–C(21)	175.8(18)	C(30)–N(30)–C(31)	175.2(23)
C(40)–N(40)–C(41)	168.3(22)		

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