

First structurally characterized mixed-halogen nickel(III) NCN-pincer complex

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ABSTRACT

A square-pyramidal mixed-halogen nickel(III) NCN-pincer complex (PipeNCN)NiClBr (where PipeNCN = 2,6-bis(piperidinomethyl)phenyl) was structurally characterized. Bromine occupies apical position; pincer ligand and chlorine atom are in the basal plane. EPR detects that complex in solution exists as a mixture of two structural isomers with bromine or chlorine atoms in the top of pyramid.

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1. Introduction

The transition metals pincer complexes attract a great attention in the various areas of organometallic and coordination chemistry [1,2]. NCN-pincer environment stabilizing a nickel(III) oxidation state and forming metal-centered paramagnetic species [3–6] were characterized by EPR. According to structural studies dihalogen nickel(III) derivatives with NCN-pincer ligand have square-pyramidal geometry [3–6]. One of halogens occupies apical position and the other one together with two nitrogens, and carbon atom of pincer fragment form basal plane. Gerard van Koten and co-workers have observed mixed-halogen adduct formed from (NCN)NiBr and CCl₄ by EPR [6]. Here we report the first structure of mixed-halogen nickel(III) NCN-pincer complex and describe the structural isomerism of this complex in solution.

2. Results and discussion

Complex (PipeNCN)NiClBr **1** (where PipeNCN = 2,6-bis(piperidinomethyl)phenyl) have been obtained by oxidation of (PipeNCN)NiBr by CuCl₂ in acetone solution. Recrystallisation from toluene allowed to obtain crystals suitable for X-ray diffractometry.

The structural study of **1** indicates the complex molecule to have a structure of the square pyramid (Fig. 1) as many other five-coordinated pincer complexes [3–5]. Obtained single crystal demonstrates bromine atom occupying apical position and chlo-

rine being in basal plane. General view of **1** is presented in Fig. 1. Selected bond lengths and angles are listed in Table 1 together with the structural data for diiodo and dichloro analogs [3–5].

Table 1 illustrates that, in general, the bond lengths and the angles of complex **1** molecule are typical for square-pyramidal Ni(III) compounds with NCN-pincer ligands [3–5]. Most structural differences arise from different ionic radii of the halogen atoms.

Complex **1** is paramagnetic. Its isotropic EPR spectrum in solution at 270 K (Fig. 2a) looks as a sum of two broad lines without distinct hyperfine structure. In the solvent glass matrix (Fig. 2b) a superposition of two anisotropic spectra of rhombic symmetry of *g*-tensors with a hyperfine splitting on the high field component is observed. According to the literature data [3,4], a hyperfine structure on the high field component appears due to the splitting on the apical halogen atom. Consequently, we can suggest a coexistence of two structural isomers: one with bromine (**1a**) and the other with chlorine (**1b**) being in the apical position. In order to avoid the mistake associated with the disproportionation reaction leading to a mixture of dibromo and dichloro species we have obtained both of them and studied their EPR spectra.

Similar to **1**, complexes (PipeNCN)NiBr₂ **2** and (PipeNCN)NiCl₂ **3** were obtained by oxidation of the corresponding monohalogen species by copper(II) salts. Isotropic EPR spectrum of **2** (Fig. 3) demonstrates a hyperfine structure on single bromine nucleus (*a*_i(Br) = 46G, *g*_i = 2.1886) with anisotropic line broadening associated with tumbling effect (*T* = 64–15m_s), whereas spectrum of **3** is a broad singlet (*g*_i = 2.2012) without any hyperfine splitting. Both anisotropic EPR spectra have the rhombic symmetry of *g*-tensors with a hyperfine splitting on the high field component (Fig. 4, Table 2). Calculated *g*_i = (*g*₁ + *g*₂ + *g*₃)/3 values for **2** and **3** and HFC con-

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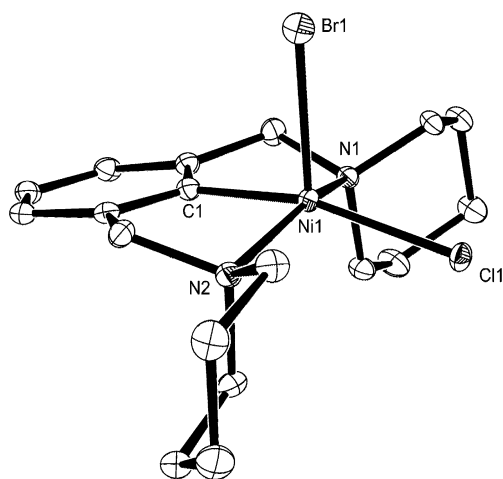


Fig. 1. Ortep view of complex **1** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

stant for **2** $a_{i(\text{Br})} = 1/3(A_{1(\text{Br})} + A_{2(\text{Br})} + A_{3(\text{Br})})$ are in a good agreement with the experimental data.

The EPR spectra shapes and the presence of additional lines in anisotropic spectrum of **2** exclude version that EPR spectrum of **1** can be the superposition of **2** and **3** spectra (Fig. 4). So, EPR spectrum of **1** is a superposition of spectra of two structural isomers differing by halogen occupying apical position. Comparison of anisotropic EPR spectra parameters of complexes **1**, **2** and **3** allows to attribute each spectra in superposition to isomer **1-a** or **1-b**, respectively (Table 2). Hyperfine coupling constants ratio on chlorine and bromine nuclei correlate with their nuclear g_N -factors ratio ($g_N(^{35}\text{Cl}/^{37}\text{Cl}) = 0.548/0.456$; $g_N(^{79}\text{Br}/^{81}\text{Br}) = 1.404/1.513$) and the hyperfine pattern is in agreement with equal nuclear spins for all isotopes ($I(^{37}\text{Cl}) = I(^{35}\text{Cl}) = I(^{79}\text{Br}) = I(^{81}\text{Br}) = 3/2$). In general, it should be mentioned that EPR spectral parameters of isomers **1a** and **1b** are very close to that measured for symmetrical di-bromo- and di-chloro- species **2** and **3**, respectively. Presence of hyperfine structure on only one bromine atom in **3** and one chlorine in **2** is in a good agreement with the viewpoint that unpaired electron is localized on the metal d_z^2 orbital. Therefore the nature of halogen lying in the basal plane of pyramid does not essentially affect the EPR spectral parameters [3,4].

The complex **1** in solution exists as a mixture of two structural isomers differing by halogen being in the top of the pyramid, although structurally studied single crystal contains only

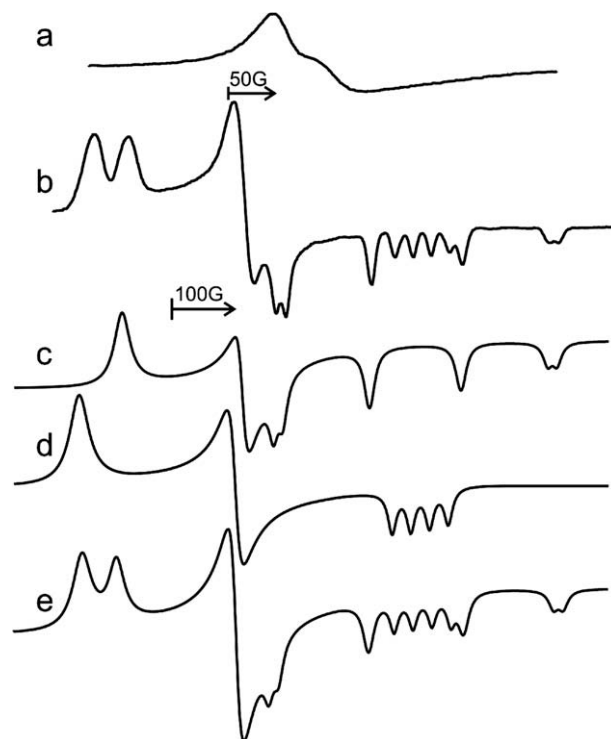


Fig. 2. An EPR spectra of **1** (toluene/ CH_2Cl_2 -solution): (a) in solution at 270K; (b) in glass matrix of solvent at 130 K; (c) simulation for Isomer **a**; (d) simulation for Isomer **b**; (e) simulation for mixture of **a** and **b** in approximately 1:1 ratio.

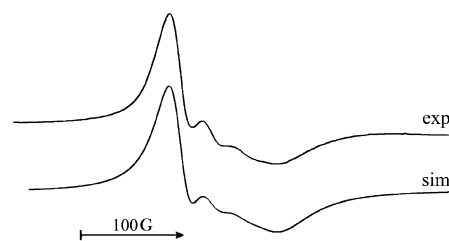


Fig. 3. EPR spectrum of **2** and its simulation (toluene, 240 K).

one of them (Isomer **1a**). Another isomer (Isomer **1b**) was not found in solid phase. The presence of the vacant site in the square-pyramidal structure allows isomers interconversion (Scheme 1). The temperature dependence of the isotropic EPR

Table 1

Selected bond lengths (Å) and angles (deg) [3–5].

Bond/angle	1a		
Ni1–C1	1.881(2)	1.898	1.885
Ni1–N1	2.056(2)	2.050	2.028
Ni1–N2	2.056(2)	2.038	2.032
Ni1– X_{basal}	2.2859(5)	2.627	2.276
Ni1– X_{apical}	2.4208(3)	2.613	2.276
C1–Ni1–N1	82.27(7)	81.89	82.14
C1–Ni1–N2	82.10(7)	82.11	82.46
N1–Ni1–N2	154.37(6)	151.97	154.05
C1–Ni1– X_{basal}	164.64(6)	168.81	164.01
C1–Ni1– X_{apical}	90.30(5)	102.95	90.98

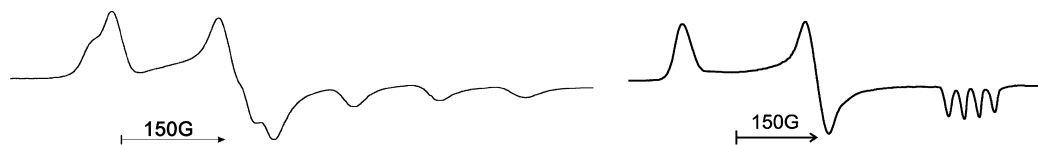


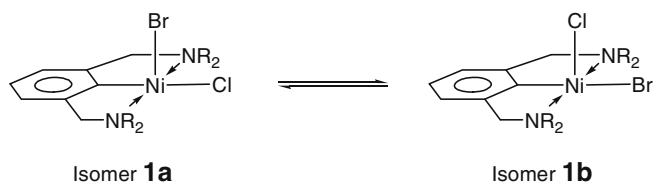
Fig. 4. EPR spectra of **2** (left) and **3** (right) (CH_2Cl_2 -toluene glass matrix at 130K).

Table 2
An EPR spectra parameters for complexes **1–3**.

Complex	g_1	g_2	g_3	A_3, G
1-a	2.341	2.204	2.029	137.0 ^a
				146.7 ^a
1-b	2.384	2.204	2.023	28.4
2	2.332	2.190	2.028	140.0 ^b
3	2.394	2.207	2.023	28.3

^a For ^{79}Br and ^{81}Br isotopes, respectively.

^b HFS on different isotopes of bromine is not observed because of broad lines.



Scheme 1. Isomers of NCN-pincer nickel complex **1**.

spectrum can be the direct proof of interconversion of isomers. Unfortunately, the isotropic spectrum of **1** cannot be uniquely interpreted due to large line width. So, we have no direct confirmation of the isomers interconversion now. However, in the isotropic spectrum of **1** (Fig. 2a) the widths of the lines are sufficiently larger than those in the spectrum of **2** (Fig. 3). Also, hyperfine structure on bromine nucleus is not resolved. With the assumption about the existence of isomers interconversion with the rates comparable with the EPR timescale, the line broadening and the decreasing of isotropic bromine HFC constant must be observed in comparison with the case of absence of the interconversion [7]. So, the difference between isotropic EPR spectra of **1** and **2** can serve as indirect evidence of the existence of the isomers interconversion.

3. Conclusions

First structurally characterized mixed-halogen nickel NCN-pincer complex has square-pyramidal geometry with bromine in the apical position and chlorine in the basal plane. EPR spectrum of solution detects two structural isomers: one with bromine and the other with chlorine in the top of pyramid.

4. Experimental section

All procedures with organometallic substances were carried out in evacuated ampoules using freshly purified solvents. EPR spectra were recorded on Bruker ER 200 D-SRC spectrometer, operating in X-band and equipped by ER 4105 DR cavity (work frequency ~ 9.5 GHz) and equipped with ER 4111 VT temperature controller. g -Factors values was determined using DPPH ($g = 2.0037$) as a standard. HFC constants values were obtained by simulation in WINEPR SimFonia (v. 1.25).

A structure of **1** was determined on Bruker Smart APEX diffractometer.

All starting substances are commercially available except described below. $(\text{DME})\text{NiBr}_2$ was obtained by reaction of nickel powder with Br_2 in dimethoxyethane.

4.1. $(\text{PipeNCN})\text{Br}$ ($\text{PipeNCN} = 2,6\text{-bis}(\text{piperidinomethyl})\text{phenyl}$)

A solution of 5 g (0.0146 mol) of $2,6\text{-(BrCH}_2)_2\text{C}_6\text{H}_3\text{Br}$ in 15 ml of benzene was slowly added to solution of 11.5 ml (9.945 g, 0.1170 mol) of piperidine in 15 ml of benzene with stirring. Then, the mixture was heated under reflux during 3 h, cooled to room temperature and kept overnight. White precipitate was filtered off and washed by benzene, the filtrate was evaporated to dryness, and crude product was recrystallized from petroleum ether forming colorless crystals. $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ/ppm): 1.55 m (12H, 6CH_2); 2.46 t (8H, $4\text{CH}_2\text{-N}$); 3.57 s (4H, $2\text{Ar-CH}_2\text{-N}$); 7.3 m (3H, C_6H_3).

4.2. $(\text{PipeNCN})\text{NiBr}$

One milliliter of 2N BuLi in hexane was added to precooled to -60°C solution of 0.7 g ($\text{PipeNCN})\text{Br}$ (1.994 mol) in Et_2O . Solution was slow warmed up to room temperature and added *in situ* to suspension of 0.4929 g (1.595 mol) of $(\text{DME})\text{NiBr}_2$ in Et_2O with stirring and kept overnight.

Orange crystals were collected after filtration, washed by cold hexane and dried in vacuum. Anal.(%) Found: C 52.73; H 6.64; Br 19.03. $\text{C}_{18}\text{H}_{27}\text{BrN}_2\text{Ni}$ Calc.: C 52.73; H 6.64; Br 19.49.

4.3. $(\text{PipeNCN})\text{NiCl}$

A solution of 0.0673 g (0.164 mmol) $(\text{PipeNCN})\text{NiBr}$ was added to a solution of 0.0352 g (0.1804 mmol) AgBF_4 in acetone. After 15 min of stirring the mixture was filtered, the filtrate was added to 0.0672 g (1.148 mmol) NaCl and the mixture was stirred over 1 h. A mixture was filtered, the filtrate was evaporated to dryness, the title product was extracted by Et_2O and used *in situ*.

4.4. $(\text{PipeNCN})\text{NiClBr}$ (1), $(\text{PipeNCN})\text{NiBr}_2$ (2), $(\text{PipeNCN})\text{NiCl}_2$ (3)

Desired product was obtained by oxidation of appropriate initial substance – $(\text{PipeNCN})\text{NiBr}$ or $(\text{PipeNCN})\text{NiCl}$ —by 5-fold excess of the corresponding dry copper di-halogenide (CuCl_2 or CuBr_2) in CH_2Cl_2 solution. Initial orange solution changes color to dark green. A solution was filtered.

$(\text{PipeNCN})\text{NiCl}_2$ was investigated without isolation. $(\text{PipeNCN})\text{NiBr}_2$ can be isolated by addition of equal volume of hexane to filtered CH_2Cl_2 solution as microcrystalline powder. $(\text{PipeNCN})\text{NiClBr}$ crystals suitable for X-ray diffractometry was obtained by slow evaporation of toluene solution.

Crystal data of complex **1**. $\text{C}_{18}\text{H}_{27}\text{BrClN}_2\text{Ni}$; $M = 445.49$; $T = 100\text{K}$; $\lambda = 0.71073 \text{ \AA}$; monoclinic, space group $\text{P2}(1)/n$; $a = 11.0519(6) \text{ \AA}$, $b = 9.8277(5) \text{ \AA}$, $c = 16.8999(9) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 91.8440(10)^\circ$, $\gamma = 90^\circ$; $V = 1834.63(17) \text{ \AA}^3$; $Z = 4$, $D_{\text{Calc}} = 1.613 \text{ g cm}^{-3}$; $F(000) = 916$; $\theta(\text{deg})$

2.17–27.50; reflections collected: 11970 unique: 4198 ($R_{\text{int}} = 0.0191$); final R indices [$I > 2\sigma(I)$] $R_1 = 0.0343$, $wR_2 = 0.1000$; R indices (all data) $R_1 = 0.0407$, $wR_2 = 0.1029$. CCDC 622274.

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