Research Article

Synthesis and Crystal Structure of *trans*-Diiodobis(piperidine-1-carbonitrile)platinum(II)

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Treatment of dichlorobis(piperidine-1-carbonitrile)platinum(II) with potassium iodide in water/methanol mixture results in the halide ligand exchange giving novel *trans*-diiodobis(piperidine-1-carbonitrile)platinum(II) complex. The reaction proceeds under mild conditions (20°C, 40 min) giving *trans*-[PtI₂(NCNC₅H₁₀)₂] in 70% isolated yield. The iodide complex was characterized by IR, ¹H and ¹³C NMR spectroscopies, and high resolution ESI-MS, and its structure was determined by a single crystal X-ray diffraction.

1. Introduction

Interest in metal complexes bearing NCR (R = Alk, Ar, NAlk₂) ligands is stimulated by enhanced reactivity of nitrile functionality in such compounds toward nucleophilic addition and 1,3-dipolar cycloaddition [1, 2]. Moreover, these metal-mediated processes allow the conductance of the reactions, which are not feasible without involvement of metal centers. Our recent results demonstrate unexpectedly high activity of platinum(II)-bound push-pull nitriles NCNAlk₂ toward cycloaddition of nitrones and nucleophilic additions [3]. Following this project focused on investigations of unusual reactivity of push-pull nitrile ligands, we studied novel platinum(II) complex bearing push-pull dialkylcyanamide ligands.

2. Materials and Methods

All reagents and solvents were obtained from commercial sources and used as received. Isomeric mixture of approximately 1:1 *cis/trans*-dichlorobis(piperidine-1-carbonitrile)platinum(II) was prepared in accordance with the published method [4]. Infrared spectrum was recorded on a Shimadzu FTIR 8400S instrument in KBr pellets. ¹H and ¹³C NMR spectra were measured on a Bruker-DPX 300 and Bruker 400 MHz Avance spectrometers at ambient

temperature. Electrospray ionization mass spectrum was obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source and MeOH was used as the solvent. The instrument was operated at positive ion mode using a *m/z* range of 50–3000.

2.1. X-Ray Crystal Structure Determination. The crystal of *trans*-[PtI₂(NCNC₅H₁₀)₂] was immersed in cryo oil, mounted in a Nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data was collected on Bruker Kappa Apex II Duo diffractometer using Mo K α radiation (λ = 0.71073 Å). The SAINT program package [5] was used for cell refinement and data reduction. The structure was solved by direct methods using SHELXS-97 [6] program with a WinGX [7] graphical user interface. A numerical absorption correction (SADABS) [8] was applied to data. Structural refinement was carried out using SHELXL-97 [6]. Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.99 and U_{iso} = 1.2·U_{eq} (parent atom). The crystallographic details are summarized in Table 1 and selected bond lengths and angles in Table 2.

2.2. Preparation of *trans*-[PtI₂(NCNC₅H₁₀)₂]. Water solution (0.5 mL) of KI (41 mg, 0.25 mmol) was added to a suspension of *cis/trans*-[PtCl₂(NCNC₅H₁₀)₂] (49 mg, 0.1 mmol) in

TABLE 1: Crystallographic details for *trans*-[PtI₂(NCNC₅H₁₀)₂].

Empirical formula	C ₁₂ H ₂₀ I ₂ N ₄ Pt
Fw	669.21
Temp. (K)	100(2)
λ (Å)	0.71073
Cryst syst	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.7497(7)
<i>b</i> (Å)	15.8212(16)
<i>c</i> (Å)	8.2773(8)
β (deg)	104.110(4)
(Å ³)	857.25(15)
<i>Z</i>	2
ρ_{calc} (Mg/m ³)	2.593
μ (Mo K α) (mm ⁻¹)	11.779
Number of reflections	27391
Unique reflections	4203
GOOF (F ²)	1.229
<i>R</i> _{int}	0.0257
<i>R</i> ^a (<i>I</i> $\geq$ 2 σ)	0.0160
<i>wR</i> ^b (<i>I</i> $\geq$ 2 σ)	0.0377

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

MeOH (0.5 mL). The reaction mixture was intensively stirred for 40 min (20–25°C) and then was left to stand at –5°C for 3 h. The resulting solid was filtered off and washed with cold methanol/water mixture (two 0.5-mL portion) and dried on air to give *trans*-[PtI₂(NCNC₅H₁₀)₂] as the light-yellow solid (47 mg, 70%).

Elemental analysis, Pt: 29.27% (29.15%, calcd). High resolution ESI⁺-MS, *m/z*: 542.0331 [M–I]⁺ (542.0381 calcd), 691.9263 [M+Na]⁺ (691.9323 calcd). IR spectrum in KBr, selected bands, cm⁻¹: 2941 s, 2864 s ν (C–H), 2293 s ν (C $\equiv$ N). ¹H NMR (300.13 MHz, CDCl₃): δ 3.32 (t, 8H, NCH₂), 1.76–1.65 (m, 8H, NCH₂CH₂), 1.65–1.56 (m, 4H, NCH₂CH₂CH₂). ¹³C{¹H} NMR (100.61 MHz, CDCl₃): δ 118.8 (NCN), 49.9 (NCH₂), 24.7 (NCH₂CH₂), 22.6 (NCH₂CH₂CH₂) (Scheme 1).

3. Results and Discussion

3.1. Synthesis of *trans*-[PtI₂(NCNC₅H₁₀)₂]. General route to iodide platinum(II) complexes bearing two neutral ligands is the exchange reaction between K₂[PtCl₄] and excess KI in water followed by reaction with neutral ligands [9–12]. In our case, this reaction was unselective and furnished the target compound in low yield with concomitant formation of the platinum black as the by-product.

Trans-diiodobis(piperidine-1-carbonitrile)platinum(II) complex (*trans*-[PtI₂(NCNC₅H₁₀)₂]) was obtained as the light-yellow solid by the reaction of dichlorobis(piperidine-1-carbonitrile)platinum(II) with potassium iodide in water/methanol mixture under mild conditions (20°C, 40 min) in 70% isolated yield. Strong *trans*-effect of iodide ligands determines the selective generation of the *trans*-isomer and

allows the use of the *cis/trans* mixture of the starting of [PtCl₂(NCNC₅H₁₀)₂] complex [4]. The advantages of this method are also mild reaction conditions, facile isolation, and high yield of the reaction product.

3.2. Characterization of *trans*-[PtI₂(NCNC₅H₁₀)₂]. In ESI⁺ mass spectrum, only two intensive signals with characteristic isotopic pattern of [M–I]⁺ and [M+Na]⁺ were detected. In IR spectrum of the title compound, the most characteristic band is from C $\equiv$ N stretching vibrations (2293 cm⁻¹). This value is higher than that in free 1-piperidinecarbonitrile (2210 cm⁻¹) [13] and is very close to ν (C $\equiv$ N) bond in *trans*-[PtCl₂(NCNC₅H₁₀)₂] (2292 cm⁻¹) [4]. In ¹H NMR, only one set of signals corresponding to the methylene groups of the piperidine ring was observed. The most characteristic signal in ¹³C NMR spectrum, sensitive to structure changes, is the one from NCN fragment at 118.8 ppm.

A single-crystal X-ray diffraction study was performed for a crystal grown by the slow evaporation of CH₂Cl₂/ⁿBu₂O (2:1, v/v) solution of *trans*-[PtI₂(NCNC₅H₁₀)₂] (Figure 1). The coordination polyhedron of the compound is formed by two piperidine-1-carbonitrile ligands in the *trans*-orientation and two iodide ligands, resulting in a typical square planar geometry.

Bond angles around the platinum(II) center are very close to 90° (89.31(5)° and 90.69(5)°). The Pt(1)–I(1) distances (2.6117(2) Å) are typical for Pt–I bonds [14, 15]. The Pt(1)–N(1) (1.9537(15) Å) bond length is equal to such bonds in similar platinum(II) complexes bearing push-pull nitriles [4, 16]. The Pt(1)–N(1)–C(1) and N(1)–C(1)–N(2) fragments are nearly linear with bond angles of 178.37(15)° and 178.1(2)°, correspondingly. The bond distance N(1)–C(1) (1.153(2) Å) is equal, within 3 σ , to the distance in similar complexes with push-pull NCNR₂ [4, 16] or with conventional NCR nitriles [17, 18]. The bond C(1)–N(2) (1.314(2) Å) is shorter than a regular single C–N bond and it is close to the typical C=N bond [19]. This could be explained by a significant contribution of the structure Pt–N[–]=C=N⁺R₂ with double bond C(1)=N(2) [20]. This data is in agreement with slightly nonlinear structure of the fragment Pt(1)–N(1)–C(1) and it is also supported by the previous investigations of complexes of similar structures [4, 16].

The angles around the N(2) atom are close to 120° varying from 116.18(13)° to 119.89(15)° thus pointing out the sp²-hybridization of the N(2) atom and the amide character of the NR₂ group. The piperidine ring has a typical chair conformation and all bond lengths are usual for single C–C bonds (ranging from 1.517(3) Å to 1.529(3) Å) [19].

4. Conclusion

The novel complex *trans*-[PtI₂(NCNC₅H₁₀)₂] bearing the push-pull nitrile ligands was prepared in high yield and characterized by IR, ¹H and ¹³C NMR spectroscopy, and high resolution ESI-MS. Proposed structure was confirmed by single crystal X-ray diffraction. The *trans*-effect of I[–] ligands determines the selective generation of *trans*-isomer.

Platinum has square planar environment with almost linear fragment Pt(1)–N(1)–C(1)–(N2). The bond length

TABLE 2: Selected bond lengths and angles (Å, °).

Pt(1)–N(1)	1.9537(15)	N(1)–Pt(1)–I(1)#1	90.69(5)
Pt(1)–I(1)	2.6117(2)	N(1)–Pt(1)–I(1)	89.31(5)
N(1)–C(1)	1.153(2)	N(1)–C(1)–N(2)	178.1(2)
N(2)–C(1)	1.314(2)	C(1)–N(1)–Pt(1)	178.37(15)
N(2)–C(6)	1.477(2)	C(1)–N(2)–C(6)	119.89(15)
N(2)–C(2)	1.478(2)	C(1)–N(2)–C(2)	117.16(15)
		C(6)–N(2)–C(2)	116.18(13)

SCHEME 1: Preparation of *trans*-[PtI₂(NCNC₅H₁₀)₂]. FIGURE 1: The molecular structure of *trans*-[PtI₂(NCNC₅H₁₀)₂], showing the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level.

C(1)–N(1) is close to double C=N bond that is caused by significant contribution of N[−]=C=N⁺R₂ structure stabilized by the platinum(II) center.

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