Research Article

¹H, ¹³C, and ¹⁵N NMR Studies of Au(III) and Pd(II) Chloride Complexes and Organometallics with 2-Acetylpyridine and 2-Benzoylpyridine

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Au(III) and Pd(II) chloride complexes with N(1),O-chelating 2-acetylpyridine (2apy) and N(1)-monodentately binding 2-benzoylpyridine (2bz'py)-[Pd(2apy)Cl₂], [Au(2bz'py)Cl₃], *trans*-[Pd(2bz'py)₂Cl₂], as well as Au(III) chloride organometallics with monoanionic forms of 2apy or 2bz'py, deprotonated at the acetyl or benzyl side groups (2apy^{*}, 2bz'py^{*})-[Au(2apy^{*})Cl₂], [Au(2bz'py^{*})Cl₂], were studied by ¹H, ¹³C, and ¹⁵N NMR. ¹H, ¹³C, and ¹⁵N coordination shifts (i.e., differences between the respective δ^{1H} , δ^{13C} , and δ^{15N} chemical shifts of the same atom in the complex and ligand molecules: $\Delta_{coord}^{1H} = \delta_{complex}^{1H} - \delta_{ligand}^{1H}$, $\Delta_{coord}^{13C} = \delta_{complex}^{13C} - \delta_{ligand}^{13C}$, $\Delta_{coord}^{15N} = \delta_{complex}^{15N} - \delta_{ligand}^{15N}$) were discussed in relation to the molecular structures and coordination modes, as well as to the factors potentially influencing nuclear shielding. Analogous NMR measurements were performed for the new (2bz'pyH)[AuCl₄] salt.

1. Introduction

2-Substituted acyl derivatives or pyridine, for example, 2-acetylpyridine (2apy) and 2-benzoylpyridine (2bz'py) (Scheme 1) can coordinate transition metal ions in several ways. In case of Au(III) and Pd(II) chloride complexes three binding modes are known: N(1)-monodentate (e.g., [Au(2bz'py)Cl₃] [1] and *trans*-[Pd(2bz'py)₂Cl₂] [2–7]), N(1),O-chelation (e.g., [Pd(2apy)Cl₂] [6]) and N(1), CH₂- or N(1),C(2')-chelation of 2apy^{*} or 2bz'py^{*} monoanionic ligands, formed by 2apy or 2bz'py deprotonation at the acetyl group or at the *ortho*-carbon within the phenyl ring (e.g., [Au(2apy^{*})Cl₂] [8] and [Au(2bz'py^{*})Cl₂] [1, 9]).

Some of these compounds exhibit catalytic properties (*trans*-[Pd(2bz'py)₂Cl₂] in hydrogenation of unsaturated functional groups [4, 5]) and biological activity ([Au(2bz'py^{*})Cl₂] is an inhibitor of cathepsin cysteine proteases [9]). Although two X-ray structures were reported for these compounds (*trans*-[Pd(2bz'py)₂Cl₂])—CCDC

782241 [7] and [Au(2bz'py^{*})Cl₂])—PUKYAV [1]; all refcodes derived from the Cambridge Structural Database [10]), they remain insufficiently characterized from the spectroscopic point of view. The ¹H NMR spectra were reported for [Au(2bz'py)Cl₃], *trans*-[Pd(2bz'py)₂Cl₂], [Au(2apy^{*})Cl₂], and [Au(2bz'py^{*})Cl₂] [1, 7–9], but in case of the two former compounds the published data are doubtful as they decompose in the applied DMSO-d₆ solvent (*vide infra*). The ¹³C NMR measurements were performed for [Au(2apy^{*})Cl₂] and [Au(2bz'py^{*})Cl₂] but without signals assignments [8, 9], while the ¹⁵N NMR spectra were never described.

In the past, we studied ¹H, ¹³C, and ¹⁵N NMR spectroscopic properties of some Au(III) and Pd(II) chloride complexes and organometallics with 2-phenylpyridine (2ppy: [Au(2ppy)Cl₃], *trans*- and *cis*-[Pd(2ppy)₂Cl₂], [Au(2ppy^{*})Cl₂] [11, 12]), using ¹H-¹³C and ¹H-¹⁵N HMQC/HMBC. Very recently, we have applied the same NMR techniques for analogous compounds

SCHEME 1: 2-acyl derivatives of pyridine: 2-acetylpyridine (2apy) and 2-benzoylpyridine (2bz'py).

with 2-benzylpyridine (2bzpy: $[\text{Au}(2\text{bzpy})\text{Cl}_3]$, *trans*- $[\text{Pd}(2\text{bzpy})_2\text{Cl}_2]$, $[\text{Au}(2\text{bzpy}^*)\text{Cl}_2]$ [13]). In this paper we report similar results for the following species: $[\text{Au}(2\text{apy}^*)\text{Cl}_2]$, $[\text{Pd}(2\text{apy})\text{Cl}_2]$, $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$, *trans*- $[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$ and $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$. Additionally, we describe the new $(2\text{bz}'\text{pyH})[\text{AuCl}_4]$ salt, analogous to that of $(2\text{bzpyH})[\text{AuCl}_4]$ (CCDC 873251 [13]).

2. Experimental

2.1. Materials. 2apy and 2bz'py (98% purity) were purchased from Fluka, Au (99.99%) from Polish Mint, and PdCl_2 (99.9%) from POCh Gliwice (Poland). Aqueous HAuCl_4 solution (ca. 0.05 M) was prepared by dissolving Au in *aqua regia* followed by the removal of HNO_3 and HCl excess by boiling. Solid NaAuCl_4 and K_2PdCl_4 were prepared in water by the reactions of HAuCl_4 with NaOH and PdCl_2 with KCl, respectively, and evaporation to dryness.

2.2. Syntheses. $[\text{Au}(2\text{apy}^*)\text{Cl}_2]$ was obtained by the method of Fan et al. (from NaAuCl_4 and 2apy) [8], $[\text{Pd}(2\text{apy})\text{Cl}_2]$ by that of Kovala-Demertzi et al. (from K_2PdCl_4 and 2apy) [6], $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$ by that of Fuchita et al. (from NaAuCl_4 and 2bz'py) [1], *trans*- $[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$ by that of Kovala-Demertzi et al. and Małeck and Maroń (from K_2PdCl_4 and 2bz'py) [6, 7], whereas $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$ by that of Zhu et al. (from NaAuCl_4 and 2bz'py in propionitrile, in the presence of $\text{CF}_3\text{SO}_3\text{Ag}$ [9]; it is worth noting that an attempt to synthesize this organometallic compound according to the report of Fuchita et al., that is, by refluxing $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$ in propionitrile in the presence of CF_3COOAg [1], has failed). The yields were ca. 60–80% for $[\text{Au}(2\text{apy}^*)\text{Cl}_2]$, $[\text{Pd}(2\text{apy})\text{Cl}_2]$, $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$, *trans*- $[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$, and ca. 25% for $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$. Their composition was confirmed by elemental analysis: $[\text{Au}(2\text{apy}^*)\text{Cl}_2]$ —C 21.9%, H 1.7%, N 3.7% (calculated for $\text{AuC}_7\text{H}_6\text{NOCl}_2$: C 21.7%, H 1.6%, N 3.6%); $[\text{Pd}(2\text{apy})\text{Cl}_2]$ —C 28.3%, H 2.5%, N 4.8% (calculated for $\text{PdC}_7\text{H}_7\text{NOCl}_2$: C 28.1%, H 2.4%, N 4.7%); $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$ —C 29.6%, H 2.3%, N 3.0% (calculated for $\text{AuC}_{12}\text{H}_9\text{NOCl}_3$: C 29.6%, H 1.9%, N 2.9%); *trans*- $[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$ —C 53.0%, H 3.3%, N 5.3% (calculated for $\text{PdC}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{Cl}_2$: C 53.0%, H 3.3%, N 5.1%); $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$ —C 32.1%, H 1.9%, N 3.2% (calculated for $\text{AuC}_{12}\text{H}_8\text{NOCl}_2$: C 32.0%, H 1.8%, N 3.1%).

Their IR spectral data were as follows: $[\text{Au}(2\text{apy}^*)\text{Cl}_2]$ — ν_{CO} 1715 cm^{-1} , ν_{AuCl} 365, 356 cm^{-1} ; $[\text{Pd}(2\text{apy})\text{Cl}_2]$ — ν_{CO} 1685 cm^{-1} , ν_{PdCl} 367, 343 cm^{-1} (368, 342 cm^{-1} [6]); $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$ — ν_{CO} 1670 cm^{-1} , ν_{AuCl} 372, 360, 353 cm^{-1} (1671 cm^{-1} and 353 cm^{-1} [1]); *trans*- $[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$ — ν_{CO} 1676 cm^{-1} , ν_{PdCl} 349 cm^{-1} (1670–1676 cm^{-1} and 345 cm^{-1} [3, 6, 7]); $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$ — ν_{CO} 1675 cm^{-1} , ν_{AuCl} 353, 302 cm^{-1} (1674–1677 cm^{-1} and 362, 300 cm^{-1} [1, 9]). The *trans*-geometry of $[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$ was proved by the presence of only one ν_{PdCl} stretching vibration (B_{2u}) typical for *trans*- MX_2Y_2 square-planar molecules (D_{2h} symmetry), in consistency with the known X-ray structure (CCDC 782241 [7]).

$(2\text{bz}'\text{pyH})[\text{AuCl}_4]$ was obtained by boiling aqueous HAuCl_4 solution with 2bz'py in ethanol (1:1; 3 h). After concentration, the overnight-formed yellow precipitate was washed with ethanol (yield ca. 90%); elemental analysis: C 28.0%, H 2.4%, N 3.2% (calculated for $\text{AuC}_{12}\text{H}_{10}\text{NOCl}_4$: C 27.6%, H 1.9%, N 2.7%). IR spectrum: ν_{CO} 1670 cm^{-1} , ν_{AuCl} 355 cm^{-1} , with these values being comparable to those for free 2bz'py (ν_{CO} 1668 cm^{-1} ; our data) and $[\text{AuCl}_4]^-$ (ν_{AuCl} 350 cm^{-1} [14]).

2.3. Spectroscopic Measurements. IR spectra were measured by a Perkin-Elmer Spectrum 2000 FT-IR spectrometer with a triglycine sulphate detector, in KBr and polyethylene for 400–400 cm^{-1} and 400–100 cm^{-1} ranges, respectively. NMR spectra were measured at 303 K in various solvents, by a Bruker Avance III 700 MHz NMR spectrometer. The ^1H - ^{13}C HMQC, ^1H - ^{13}C HMBC and ^1H - ^{15}N HMBC experiments were adjusted for $^1J_{\text{H-C}} = 150 \text{ Hz}$, $^nJ_{\text{H-C}} = 10 \text{ Hz}$, $^nJ_{\text{H-N}} = 5 \text{ Hz}$, with the following parameters: $\pi/2$ pulse lengths for ^1H : 9–10 μs , ^{13}C : 12–13 μs , ^{15}N : 23–24 μs ; acquisition time for ^1H - ^{13}C HMQC and HMBC: 0.2–0.3 s, for ^1H - ^{15}N HMBC: 0.07–0.08 s; relaxation delay for ^1H - ^{13}C HMQC and HMBC: 1.5 s, for ^1H - ^{15}N HMBC: 2 s. As references were used: TMS for ^1H and ^{13}C (with residual ^1H and ^{13}C solvent signals as primary references—in CDCl_3 : 7.24 ppm and 77.2 ppm, in CD_2Cl_2 : 5.32 ppm and 54.0 ppm, in CD_3CN : 1.94 ppm and 1.4 ppm, in $\text{DMSO}-d_6$: 2.50 ppm and 39.5 ppm); neat nitromethane for ^{15}N .

3. Results and Discussion

3.1. IR Spectroscopy. The shift of the C=O stretching vibration absorption band is sometimes used to determine the coordination mode in 2-acylpyridines complexes; thus we have tested this method for the studied known 2apy/2apy* and 2bz'py/2bz'py* compounds. In fact, the comparison of their IR spectra to those for free ligands reveals the ν_{CO} decrease in $[\text{Pd}(2\text{apy})\text{Cl}_2]$ (1700 $\text{cm}^{-1} \rightarrow 1685 \text{ cm}^{-1}$) and the ν_{CO} increase in $[\text{Au}(2\text{apy}^*)\text{Cl}_2]$ (1700 $\text{cm}^{-1} \rightarrow 1715 \text{ cm}^{-1}$) or $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$, *trans*- $[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$, $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$ (1668 $\text{cm}^{-1} \rightarrow 1670, 1676, 1675 \text{ cm}^{-1}$). Such a difference might indicate the presence or absence

TABLE 1: ^1H chemical and coordination/protonation shifts (in parentheses) for Au(III) and Pd(II) chloride complexes, organometallics, and salts with 2apy or 2bz'py.

Compound	H(3)	H(4)	H(5)	H(6)	H(2')	H(3')	H(4')	H(5')	H(6')	CH_n
2apy ^{DMSO-d₆}	7.93	7.98	7.64	8.71						CH_3 2.62
[Au(2apy*)Cl ₂] ^{DMSO-d₆ a}	8.10 (+0.17)	8.55 (+0.57)	8.17 (+0.53)	9.63 (+0.92)						CH_2 3.72 (+1.10)
2bz'py ^{CDCl₃}	8.03	7.89	7.45	8.71	8.05	7.48	7.58			
2bz'py ^{CD₂Cl₂}	8.03	7.92	7.49	8.70	8.04	7.50	7.61			
2bz'py ^{CD₃CN}	7.98	8.00	7.57	8.68	8.01	7.51	7.63	as H(3')	as H(2')	
2bz'py ^{DMSO-d₆}	8.00	8.08	7.67	8.73	7.97	7.55	7.69			
[Au(2bz'py)Cl ₃] ^{CDCl₃}	7.96 (−0.07)	8.27 (+0.38)	7.91 (+0.46)	9.10 (+0.39)	7.86 (−0.19)	7.56 (+0.08)	7.72 (+0.14)			
[Au(2bz'py)Cl ₃] ^{CD₂Cl₂}	8.25 (+0.22)	8.44 (+0.52)	8.01 (+0.52)	9.03 (+0.33)	7.98 (−0.06)	7.60 (+0.10)	7.74 (+0.13)	as H(3')	as H(2')	
[Au(2bz'py)Cl ₃] ^{CD₃CN}	8.37 (+0.39)	8.70 (+0.70)	8.23 (+0.66)	8.90 (+0.22)	7.95 (−0.06)	7.60 (+0.09)	7.84 (+0.21)			
<i>trans</i> -Pd(2bz'py) ₂ Cl ₂ ^{CDCl₃}	7.62 (−0.41)	7.83 (−0.06)	7.33 (−0.12)	8.27 (−0.44)	8.00 (−0.05)	7.57 (+0.09)	7.67 (+0.04)			
<i>trans</i> -Pd(2bz'py) ₂ Cl ₂ ^{CD₂Cl₂}	7.63 (−0.40)	7.90 (−0.02)	7.38 (−0.11)	8.23 (−0.47)	7.96 (−0.08)	7.60 (+0.10)	7.73 (+0.12)	as H(3')	as H(2')	
<i>trans</i> -Pd(2bz'py) ₂ Cl ₂ ^{CD₃CN}	7.67 (−0.31)	8.01 (+0.01)	7.50 (−0.07)	8.26 (−0.42)	7.90 (−0.11)	7.61 (+0.10)	7.77 (+0.14)			
[Au(2bz'py*)Cl ₂] ^{CD₂Cl₂}	8.36 (+0.33)	8.37 (+0.45)	7.89 (+0.40)	9.58 (+0.88)		7.88 (+0.38)	7.47 (−0.14)	7.45 (−0.05)	7.77 (−0.27)	
[Au(2bz'py*)Cl ₂] ^{CD₃CN}	8.32 (+0.34)	8.43 (+0.43)	7.93 (+0.36)	9.49 (+0.81)	no proton	7.84 (+0.33)	7.46 (−0.17)	7.46 (−0.05)	7.74 (−0.27)	
[Au(2bz'py*)Cl ₂] ^{DMSO-d₆ b}	8.37 (+0.37)	8.56 (+0.48)	8.09 (+0.42)	9.48 (+0.75)		7.77 (+0.22)	7.49 (−0.20)	7.47 (−0.08)	7.69 (−0.28)	
(2bz'pyH)[AuCl ₄] ^{CD₃CN}	8.35 (+0.37)	8.69 (+0.69)	8.22 (+0.65)	8.89 (+0.21)	7.93 (−0.08)	7.64 (+0.13)	7.80 (+0.17)			

Literature data for ^1H [Au(2apy*)Cl₂] in DMSO-d₆: 9.62, 8.55, 8.17, 8.08, 3.72 ppm (unassigned) [8] and ^1H [Au(2bz'py*)Cl₂] in DMSO-d₆: 9.48-H(6), 8.56-H(4), 8.37-H(3), 8.09-H(5), 2×7.65 – 7.73 , 2×7.40 – 7.55 ppm (unassigned) [1]; 9.47, 8.54, 8.36, 8.09, 2×7.66 – 7.76 , 2×7.42 – 7.50 ppm (unassigned) [9].

of the coordination bonding between the carbonyl group and the metal atom; however, our review of the literature of the IR data for some other 2apy/2apy* and 2bz'py/2bz'py* species has suggested this criterion is uncertain—even for the complexes having the same coordination sphere the ν_{CO} changes are variable (e.g., 16 cm^{-1} decrease for [Ag(2apy-N¹, CO)₂] CF₃SO₃—PURYOR [15]: $1700\text{ cm}^{-1} \rightarrow 1684\text{ cm}^{-1}$ [15] versus 0 cm^{-1} change for [Ag(2apy-N¹, CO)₂] ClO₄—RAWVAN, RAWVAN01 [16, 17]: $1700\text{ cm}^{-1} \rightarrow 1700\text{ cm}^{-1}$ [16]). Thus, much a better tool for such studies is NMR spectroscopy.

3.2. ^1H NMR Spectroscopy. [Au(2apy*)Cl₂] and [Pd(2apy)Cl₂] are insoluble in CDCl₃, CD₂Cl₂, and CD₃CN, but soluble in DMSO-d₆. However, [Au(2apy*)Cl₂] is stable in the latter solvent, whereas [Pd(2apy)Cl₂] immediately decomposes to free 2apy, with its solubility in the other media (e.g., DMF-d₇) being insufficient even for ^1H NMR

measurements. For all studied compounds, the ^1H chemical and coordination shifts are collected in Table 1.

The ^1H NMR spectral pattern of the [Au(2apy*)Cl₂] organometallic corresponds well to the N(1),CH₂-cyclometallated structure, revealing 5 proton resonances (2 doublets: H(3), H(6); 2 triplets: H(4), H(5); 1 singlet: CH₂). The heterocyclic ring protons are significantly deshielded (mean $\Delta_{\text{coord}}^{\text{H(3)}-\text{H(6)}}$ value: 0.55 ppm), with the largest effect concerning the nitrogen-adjacent H(6) proton ($\Delta_{\text{coord}}^{\text{H(6)}} = 0.92\text{ ppm}$); high deshielding occurs also for the deprotonated acetyl group ($\Delta_{\text{coord}}^{\text{CH}_2} = 1.10\text{ ppm}$). The reason is probably an inductive effect of two electronegative chlorides and, in case of the acetyl substituent, the CH₃ $\rightarrow$ CH₂ transition followed by metallation of the respective carbon.

The review of NMR data for some other d⁸ square-planar transition metal ions reveals similarly large H(6) and CH₂ deshielding effects in N(1), CH₂-chelated 2apy* organometallics (e.g., for [Pd(2apy*)(P(C₆H₅)₃)Cl] in CDCl₃: $\Delta_{\text{coord}}^{\text{H(6)}} = 0.88\text{ ppm}$, $\Delta_{\text{coord}}^{\text{CH}_2} = 1.38\text{ ppm}$, as

TABLE 2: ^{13}C chemical and coordination/protonation shifts (in parentheses) for Au(III) and Pd(II) chloride complexes, organometallics and salts with 2apy or 2bz'py.

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C(1')	C(2')	C(3')	C(4')	C(5')	C(6')	CO	CH _n
2apy ^{DMSO-d₆}	152.9	121.0	137.4	127.6	149.1							199.4	^{CH₃} 25.5
[Au(2apy*)Cl ₂] ^{DMSO-d₆ a}	150.1 (-2.8)	126.1 (+5.1)	144.2 (+6.8)	131.4 (+3.8)	148.0 (-1.1)							197.2 (-2.2)	^{CH₂} 57.7 (+32.2)
2bz'py ^{CDCl₃}	155.2	124.7	137.2	126.3	148.7	136.4	131.1	128.3	133.0			194.0	
2bz'py ^{CD₂Cl₂}	155.4	124.6	137.3	126.5	148.8	136.8	131.2	128.3	133.0			194.0	
2bz'py ^{CD₃CN}	156.1	125.2	138.4	127.5	149.6	137.7	131.8	129.1	133.8			195.0	
2bz'py ^{DMSO-d₆}	154.5	124.1	137.6	126.7	148.5	136.0	130.6	128.1	132.9			193.4	
[Au(2bz'py)Cl ₃] ^{CDCl₃}	153.8 (-1.4)	129.9 (+5.2)	142.4 (+5.2)	129.9 (+3.6)	152.6 (+3.9)	n.d.	131.2 (+0.1)	129.4 (+1.1)	135.3 (+2.3)			n.d.	
<i>trans</i> -[Pd(2bz'py) ₂ Cl ₂] ^{CDCl₃}	157.5 (+2.3)	127.4 (+2.7)	139.0 (+1.8)	126.6 (+0.3)	153.6 (+4.9)	n.d.	132.0 (+0.9)	128.7 (+0.4)	133.7 (+0.7)			191.8 (-2.2)	
[Au(2bz'py*)Cl ₂] ^{CD₂Cl₂}	146.8 (-8.6)	127.7 (+3.1)	143.9 (+6.6)	129.9 (+3.4)	152.3 (+3.5)	128.3 (-8.5)	138.5 (+7.3)	134.4 (+6.1)	134.2 (+1.2)	129.3 (+1.0)	130.6 (-0.6)	189.5 (-4.5)	
[Au(2bz'py*)Cl ₂] ^{DMSO-d₆ b}	145.1 (-9.4)	127.1 (+3.0)	144.3 (+6.7)	129.6 (+2.9)	152.7 (+4.2)	127.7 (-8.3)	136.7 (+6.1)	133.9 (+5.8)	133.2 (+0.3)	128.6 (+0.5)	129.9 (-0.7)	188.7 (-4.7)	
(2bz'pyH)[AuCl ₄] ^{CD₃CN}	n.d.	130.5 (+5.3)	149.3 (+10.9)	131.5 (+4.0)	144.7 (-4.9)	134.6 (-3.1)	131.4 (-0.4)	130.2 (+1.1)	136.0 (+2.2)			187.9 (-7.1)	

Literature data for ¹³Au(2apy*)Cl₂ in DMSO-d₆: 147.8, 144.1, 131.3, 126.0, 57.7 ppm (unassigned, quaternary carbon lacking) and ¹³[Au(2bz'py*)Cl₂] in DMSO-d₆: 127.1, 127.8, 128.6, 129.6, 129.9, 133.2, 134.0, 136.7, 144.3, 145.1, 152.8, 188.7 ppm (unassigned) [9].

TABLE 3: ^{15}N chemical and coordination/protonation shifts (in parentheses) for Au(III) and Pd(II) chloride complexes, organometallics, and salts with 2apy or 2bz'py.

Compound	N(1)
2apy ^{DMSO-d₆}	-62.4
[Au(2apy*)Cl ₂] ^{DMSO-d₆}	-156.5 (-94.1)
2bz'py ^{CDCl₃}	-61.4
2bz'py ^{DMSO-d₆}	-60.3
2bz'py ^{CD₃CN}	-60.3
[Au(2bz'py)Cl ₃] ^{CDCl₃}	-148.7 (-87.3)
<i>trans</i> -[Pd(2bz'py) ₂ Cl ₂] ^{CDCl₃}	-164.9 (-103.5)
[Au(2bz'py*)Cl ₂] ^{DMSO-d₆}	-165.0 (-104.7)
(2bz'pyH)[AuCl ₄] ^{CD₃CN}	-171.4 (-111.1)

$\delta^{\text{H}(6)} = 9.57$ ppm, $\delta^{\text{CH}_2} = 4.11$ ppm [18]), whereas in N(1), O-chelated 2apy complexes they occurred only for H(6) but not for CH₃ (e.g., for [Rh(2apy)(CO)Cl], [Rh(2apy)(COCH₃)Cl], and [Rh(2apy)(COC₂H₅)Cl] in CDCl₃: $\Delta_{\text{coord}}^{\text{H}(6)} = 0.46$ –0.54 ppm, $\Delta_{\text{coord}}^{\text{CH}_3} = -0.13$ to -0.10 ppm, as $\delta^{\text{H}(6)} = 9.15$ –9.23 ppm, $\delta^{\text{CH}_3} = 2.60$ –2.63 ppm [19]); free 2apy in CDCl₃: $\delta^{\text{H}(6)} = 8.69$ ppm, $\delta^{\text{CH}_3} = 2.73$ ppm [20].

The [Au(2bz'py)Cl₃] and *trans*-[Pd(2bz'py)₂Cl₂] complexes are soluble and stable in CDCl₃, CD₂Cl₂, and CD₃CN. In all solvents, the latter molecule exhibits no rotational isomerism even upon cooling to -40°C ; the only changes concern the H(6) peak, appearing at 20°C as a broadened singlet ($\nu_{1/2} = \text{ca. } 20$ Hz)

and becoming at 0°C a well-shaped multiplet. The occurrence of *trans*-[Pd(2bz'py)₂Cl₂] in one form only is surprising as for many other *trans*-[PdL₂Cl₂] complexes with 2-alkyl- or 2-arylpyridines (L = 2-methylpyridine [21], 2,3-dimethylpyridine and 2,4-dimethylpyridine [22], 2-(2-chloroethyl)pyridine [23], 2bzpy [13, 24], and 2-(1-methylbenzyl)pyridine [25]) two distinct rotamers were observed by ¹H NMR, even at ambient conditions. Most likely, in case of *trans*-[Pd(2bz'py)₂Cl₂] the steric hindrance allows for one stable conformation only, analogous to that known from the solid phase (CCDC 782241 [7]), that is, with phenyl rings in both 2bz'py molecules positioned at the largest distance.

For [Au(2bz'py)Cl₃] the pyridine ring protons are moderately deshielded (mean $\Delta_{\text{coord}}^{\text{H}(3)-\text{H}(6)}$: 0.29–0.49 ppm, depending on the solvent), similarly to [Au(2ppy)Cl₃] and [Au(2bzpy)Cl₃] (mean $\Delta_{\text{coord}}^{\text{H}(3)-\text{H}(6)}$: 0.36 ppm and 0.32 ppm, both in CDCl₃ [11, 13]). However, H(6) deshielding is larger than in both latter complexes ($\Delta_{\text{coord}}^{\text{H}(6)}$: 0.22–0.39 ppm versus 0.15 ppm and 0.14 ppm [11, 13]).

For *trans*-[Pd(2bz'py)₂Cl₂] the pyridine ring protons are moderately shielded (mean $\Delta_{\text{coord}}^{\text{H}(3)-\text{H}(6)}$: from -0.26 to -0.19 ppm, depending on the solvent), in contrast to *trans*-[Pd(2ppy)₂Cl₂] and *trans*-[Pd(2bzpy)₂Cl₂], where they were variously affected (mean $\Delta_{\text{coord}}^{\text{H}(3)-\text{H}(6)}$: -0.04 ppm and 0.10 ppm, both in CDCl₃ [11, 13]). In CDCl₃, a relatively large H(6) shielding contrasts to much weaker effect for *trans*-[Pd(2ppy)₂Cl₂] and the deshielding for *trans*-[Pd(2bzpy)₂Cl₂] ($\Delta_{\text{coord}}^{\text{H}(6)}$: -0.44 ppm versus -0.12 ppm and 0.44 ppm [11, 13]).

The differences between both complexes are probably caused by the fact that in $[\text{Au}(\text{2bz}'\text{py})\text{Cl}_3]$ an inductive deshielding effect of three chlorides is present only, while in *trans*- $[\text{Pd}(\text{2bz}'\text{py})_2\text{Cl}_2]$ an analogous influence of two chlorides is overcome by anisotropic interactions of the adjacent heterocyclic rings, which can either increase or decrease ^1H shielding constants, depending on the orientation of all π -electron ring systems. The variations of an anisotropic effect caused by the C=O double bond must be also taken into account.

In both complexes the changes for phenyl ring protons are of variable sign and small absolute magnitude (mean $\Delta_{\text{coord}}^{\text{H}(2')-\text{H}(6')}$: -0.02 to 0.05 ppm for $[\text{Au}(\text{2bz}'\text{py})\text{Cl}_3]$, 0.02 – 0.05 ppm for *trans*- $[\text{Pd}(\text{2bz}'\text{py})_2\text{Cl}_2]$, depending on the solvent). On average, all heterocyclic ring protons in $[\text{Au}(\text{2bz}'\text{py})\text{Cl}_3]$ are deshielded (mean $\Delta_{\text{coord}}^{\text{H}(3)-\text{H}(6),\text{H}(2')-\text{H}(6')}$: 0.12 – 0.25 ppm), while in *trans*- $[\text{Pd}(\text{2bz}'\text{py})_2\text{Cl}_2]$ they are shielded (mean $\Delta_{\text{coord}}^{\text{H}(3)-\text{H}(6),\text{H}(2')-\text{H}(6')}$: -0.10 to -0.06 ppm).

In DMSO- d_6 both complexes immediately decompose, yielding uncoordinated $\text{2bz}'\text{py}$, as their NMR spectra are identical with that for the free ligand; it is worth noting that some previous authors reported the ^1H chemical shifts for $[\text{Au}(\text{2bz}'\text{py})\text{Cl}_3]$ [1] and *trans*- $[\text{Pd}(\text{2bz}'\text{py})_2\text{Cl}_2]$ [7] just in this NMR solvent, assuming they concerned the complex molecules, although they were nearly the same as for $\text{2bz}'\text{py}$. This problem is often for Au(III) and Pd(II) chloride-azine complexes, as exemplified by $[\text{Au}(\text{2bzpy})\text{Cl}_3]$ and *trans*- $[\text{Pd}(\text{2bzpy})_2\text{Cl}_2]$ [13].

The $[\text{Au}(\text{2bz}'\text{py}^*)\text{Cl}_2]$ organometallic is insoluble in CDCl_3 but soluble in some other NMR solvents: slightly in CD_3CN , moderately in CD_2Cl_2 , and well in DMSO- d_6 , where, in contrast to $[\text{Au}(\text{2bz}'\text{py})\text{Cl}_3]$, it does not decompose. A similar behavior was reported for $[\text{Au}(\text{LL}^*)\text{Cl}_2]$ organometallics with many other 2-arylpyridines ($\text{LL} = \text{2ppy}$ [12, 26–28], 2bzpy [13, 29, 30], 2-phenoxy pyridine and 2-phenylsulfanylpyridine [31], 2-phenylaminopyridine, and 2-phenyl(*N*-methyl)aminopyridine [31, 32]).

In all solvents the ^1H NMR pattern of $[\text{Au}(\text{2bz}'\text{py}^*)\text{Cl}_2]$ corresponds well to the N(1),C(2')-cyclometallated structure, revealing 8 proton resonances (4 doublets: H(3), H(6), H(3'), H(6') and 4 triplets: H(4), H(5), H(4'), H(5')), with the absence of H(2') and inequivalency of all other phenyl ring hydrogens. The pyridine ring protons are significantly deshielded (mean $\Delta_{\text{coord}}^{\text{H}(3)-\text{H}(6)}$ value: 0.48 – 0.52 ppm, depending on the solvent), with the largest effect occurring for H(6) ($\Delta_{\text{coord}}^{\text{H}(6)} = 0.75$ – 0.88 ppm versus $\Delta_{\text{coord}}^{\text{H}(3)} - \Delta_{\text{coord}}^{\text{H}(5)} = 0.33$ – 0.48 ppm, depending on the solvent). In CDCl_3 , the H(6) deshielding is much larger than for $[\text{Au}(\text{2bz}'\text{py})\text{Cl}_3]$ ($\Delta_{\text{coord}}^{\text{H}(6)}$: 0.88 ppm versus 0.39 ppm); the same $\Delta_{\text{coord}}^{\text{H}(6)}[\text{Au}(\text{LL}^*)\text{Cl}_2] > \Delta_{\text{coord}}^{\text{H}(6)}[\text{Au}(\text{LL})\text{Cl}_3]$ relation was noted in various media for $[\text{Au}(\text{2ppy}^*)\text{Cl}_2]$ and $[\text{Au}(\text{2ppy})\text{Cl}_3]$ (0.86 – 0.87 ppm versus 0.15 ppm [11, 12, 26–28]), as well as for $[\text{Au}(\text{2bzpy}^*)\text{Cl}_2]$ and $[\text{Au}(\text{2bzpy})\text{Cl}_3]$ (0.66 – 0.79 ppm versus 0.00 – 0.33 ppm [13, 29, 30]). In DMSO- d_6 , H(6)

deshielding is close to $[\text{Au}(\text{2ppy}^*)\text{Cl}_2]$ and $[\text{Au}(\text{2bzpy}^*)\text{Cl}_2]$ ($\Delta_{\text{coord}}^{\text{H}(6)}$: 0.75 ppm versus 0.86 – 0.87 ppm [12, 26–28] and 0.69 ppm [13, 30]). It seems to be related to the presence of chlorides in the Au(III) coordination sphere, because in $[\text{Au}(\text{2bz}'\text{py}^*)_2]^+$ cations this proton was shielded ($\Delta_{\text{coord}}^{\text{H}(6)} = -0.29$ ppm, as $\delta^{\text{H}(6)} = 8.44$ ppm, in DMSO- d_6 , BF_4^- counterions [1]).

The changes for phenyl ring protons in $[\text{Au}(\text{2bz}'\text{py}^*)\text{Cl}_2]$ are of variable sign and moderate or small absolute magnitude, although rather shielding (mean $\Delta_{\text{coord}}^{\text{H}(3')-\text{H}(6')}$: from -0.08 to -0.02 ppm, depending on the solvent). The H(3') atom, adjacent to the metallated C(2') carbon, is moderately deshielded while the other protons are weakly shielded ($\Delta_{\text{coord}}^{\text{H}(3')} = 0.22$ – 0.38 ppm versus $\Delta_{\text{coord}}^{\text{H}(4')} - \Delta_{\text{coord}}^{\text{H}(6')} = -0.28$ to -0.05 ppm, depending on the solvent). In DMSO- d_6 , the same dependency was observed for $[\text{Au}(\text{2ppy}^*)\text{Cl}_2]$ ($\Delta_{\text{coord}}^{\text{H}(3')} = 0.36$ ppm versus $\Delta_{\text{coord}}^{\text{H}(4')} - \Delta_{\text{coord}}^{\text{H}(6')} = -0.11$ to 0.02 ppm [12]) and $[\text{Au}(\text{2bzpy}^*)\text{Cl}_2]$ ($\Delta_{\text{coord}}^{\text{H}(3')} = 0.13$ ppm versus $\Delta_{\text{coord}}^{\text{H}(4')} - \Delta_{\text{coord}}^{\text{H}(6')} = -0.11$ to -0.02 ppm [13]). On average, all heterocyclic ring protons in $[\text{Au}(\text{2bz}'\text{py}^*)\text{Cl}_2]$ are moderately deshielded (mean $\Delta_{\text{coord}}^{\text{H}(3)-\text{H}(6),\text{H}(3')-\text{H}(6')}$ value: 0.21 – 0.25 ppm, depending on the solvent), again similarly to $[\text{Au}(\text{2ppy}^*)\text{Cl}_2]$ and $[\text{Au}(\text{2bzpy}^*)\text{Cl}_2]$ (mean $\Delta_{\text{coord}}^{\text{H}(3)-\text{H}(6),\text{H}(3')-\text{H}(6')}$: 0.30 ppm and 0.23 – 0.30 ppm [12, 13]).

The $(\text{2bz}'\text{pyH})[\text{AuCl}_4]$ salt is insoluble in CDCl_3 and CD_2Cl_2 but soluble in CD_3CN . In the latter solvent its ^1H NMR spectrum is noticeably different from that of unprotonated $\text{2bz}'\text{py}$; however, addition of the free ligand results in only one set of ^1H signals at intermediate chemical shifts, indicating fast proton exchange between $\text{2bz}'\text{pyH}^+$ and $\text{2bz}'\text{py}$. In DMSO- d_6 it immediately decomposes yielding unprotonated $\text{2bz}'\text{py}$, probably due to the hydrolysis of $\text{2bz}'\text{pyH}^+$ cations by residual water (in the past we determined its amount in this NMR solvent by the Karl-Fischer method, as *ca.* 0.05% by weight [33]). It is worth noting that analogous 2bzpyH^+ cations (from $(\text{2bzpyH})[\text{AuCl}_4]$ —CCDC 873251) remained protonated in DMSO- d_6 [13], which suggests that $\text{2bz}'\text{py}$ is a weaker base than 2bzpy .

In CD_3CN the $\text{2bz}'\text{py}$ protonation results in the moderate ^1H deshielding effect (mean $\Delta_{\text{prot}}^{\text{H}(3)-\text{H}(6),\text{H}(2')-\text{H}(6')}$ for $\text{2bz}'\text{pyH}^+$: 0.24 ppm), much stronger for the pyridine ring (mean $\Delta_{\text{prot}}^{\text{H}(3)-\text{H}(6)}$: 0.48 ppm) than the phenyl one (mean $\Delta_{\text{prot}}^{\text{H}(2')-\text{H}(6')}$: 0.05 ppm). The deshielding of H(6) is weaker than for more far-distant pyridine ring protons ($\Delta_{\text{prot}}^{\text{H}(6)} = 0.21$ ppm versus $\Delta_{\text{prot}}^{\text{H}(3)} - \Delta_{\text{prot}}^{\text{H}(5)} = 0.37$ – 0.69 ppm). The same effects and dependencies were noted in various solvents for $(\text{2bzpyH})[\text{AuCl}_4]$ (mean $\Delta_{\text{prot}}^{\text{H}(3)-\text{H}(6),\text{H}(2')-\text{H}(6')}$: 0.28 – 0.35 ppm; mean $\Delta_{\text{prot}}^{\text{H}(3)-\text{H}(6)}$: 0.53 – 0.66 ppm versus mean $\Delta_{\text{prot}}^{\text{H}(2')-\text{H}(6')}$: 0.08 – 0.11 ppm; $\Delta_{\text{prot}}^{\text{H}(6)} = 0.00$ – 0.33 ppm versus $\Delta_{\text{prot}}^{\text{H}(3)} - \Delta_{\text{prot}}^{\text{H}(5)} = 0.58$ – 0.83 ppm [13]).

3.3. ^{13}C and ^{15}N NMR Spectroscopy. ^{13}C and ^{15}N NMR chemical and coordination/protonation shifts for all studied species (except for $[\text{Pd}(\text{2apy})\text{Cl}_2]$) are collected in Tables 2 and 3, respectively.

In $[\text{Au}(\text{2apy}^*)\text{Cl}_2]$ the nitrogen-adjacent C(2) and C(6) atoms are shielded up to ca. 3 ppm, while the other heterocyclic carbons are deshielded up to ca. 7 ppm; the average effect for the whole pyridine ring is deshielding (mean $\Delta_{\text{coord}}^{\text{C}(2)-\text{C}(6)}$ value: 2.4 ppm). The Au-bonded acetyl carbon is deshielded by as much as ca. 32 ppm, whereas the uncoordinated carbonyl group remains nearly unaffected (shielding by ca. 2 ppm), which confirms the suggested N(1), CH_2 -chelation mode.

The Au(III) or Pd(II) complexation of $2\text{bz}'\text{py}$ results in the predominant deshielding of pyridine ring carbons, up to ca. 5 ppm; the average effects (mean $\Delta_{\text{coord}}^{\text{C}(2)-\text{C}(6)}$: 3.3 ppm for $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$ and 2.4 ppm for $\text{trans}-[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$) are nearly exactly the same like for $[\text{Au}(2\text{bzpy})\text{Cl}_3]$ (3.2 ppm) and $\text{trans}-[\text{Pd}(2\text{bzpy})_2\text{Cl}_2]$ (2.4 ppm) [13]. Within the phenyl ring, the quarternary C(1') atoms have not been detected, while those of C(2')-C(6') are deshielded, up to ca. 2 ppm and up to ca. 1 ppm, respectively.

For $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$ the changes are variable. The coordinated C(2') atom is deshielded by ca. 6–7 ppm only, with this phenomenon being weaker than for $[\text{Au}(2\text{bzpy}^*)\text{Cl}_2]$ (ca. 12–13 ppm) [13] and $[\text{Au}(2\text{ppy}^*)\text{Cl}_2]$ (ca. 26 ppm) [12]. So large differences between relatively similar compounds are probably caused by the fact that C(2') deshielding is the overall result of carbon deprotonation and its subsequent auration, both effects being of opposite sign and comparable magnitude. The other heterocyclic carbons are variously affected: the quaternary C(2) and C(1') atoms are shielded by ca. 8–9 ppm, while the CH ones are rather deshielded, up to ca. 7 ppm. On average, the ^{13}C deshielding is noted (pyridine ring—mean $\Delta_{\text{coord}}^{\text{C}(2)-\text{C}(6)}$: 1.5–1.6 ppm; phenyl ring—mean $\Delta_{\text{coord}}^{\text{C}(1')-\text{C}(6')}$: 0.6–1.1 ppm; both heterocyclic rings—mean $\Delta_{\text{coord}}^{\text{C}(2)-\text{C}(6), \text{C}(1')-\text{C}(6')}$: 1.0–1.3 ppm). The carbonyl group is shielded by ca. 5 ppm.

The protonation of $2\text{bz}'\text{py}$ results in variable effects within both heterocyclic rings: from ca. 5 ppm shielding of C(6) to ca. 11 ppm deshielding of C(4) (the C(2) signal was not detected); a similarly complicated ^{13}C NMR pattern was noted for 2bzpyH^+ cations [13]. The carbonyl group is surprisingly shielded by as much as ca. 7 ppm, which may suggest its partial protonation and an equilibrium between N(1)- and CO-protonated forms of $2\text{bz}'\text{pyH}^+$.

The Au(III) or Pd(II) complexation of $2\text{bz}'\text{py}$ results in large N(1) with shielding, this effect being ca. 16 ppm weaker for $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$ than $\text{trans}-[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$, as illustrated by absolute magnitudes of the ^{15}N coordination shifts ($|\Delta_{\text{coord}}^{\text{N}(1)}|$: 87.3 ppm versus 103.5 ppm). The same dependency was noted for many other $[\text{AuLCl}_3]$ and $\text{trans}-[\text{PdL}_2\text{Cl}_2]$ complexes with N(1)-monodentately bonded azines (L = pyridine; 2-, 3-, 4-methylpyridine; 2,3-, 2,4-, 2,6-, 3,5-dimethylpyridine; 2,4,6-trimethylpyridine; 2-,

3-, 4-phenylpyridine; 2bzpy [11, 13, 21, 22, 34, 35]). Generally, for 2-arylpyridines the $|\Delta_{\text{coord}}^{\text{N}(1)}|$ parameters decrease in the $2\text{bz}'\text{py} \rightarrow 2\text{bzpy} \rightarrow 2\text{ppy}$ order: 87.3 ppm $\rightarrow$ 83.9 ppm $\rightarrow$ 77.6 ppm for $[\text{AuLCl}_3]$ and 103.5 ppm $\rightarrow$ 94.4 ppm $\rightarrow$ 90.4 ppm for $\text{trans}-[\text{PdL}_2\text{Cl}_2]$ [11, 13].

In $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$ the N(1) atom is ca. 17 ppm more shielded than in $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$ ($|\Delta_{\text{coord}}^{\text{N}(1)}|$: 104.7 ppm versus 87.3 ppm), with this difference being much larger than in case of similar pairs $[\text{Au}(2\text{bzpy}^*)\text{Cl}_2]$ – $[\text{Au}(2\text{bzpy})\text{Cl}_3]$ (90.9 ppm versus 83.9 ppm) [13] and $[\text{Au}(2\text{ppy}^*)\text{Cl}_2]$ – $[\text{Au}(2\text{ppy})\text{Cl}_3]$ (77.0 ppm versus 77.6 ppm) [11, 12]. For all studied $[\text{Au}(\text{LL}^*)\text{Cl}_2]$ organometallics the $|\Delta_{\text{coord}}^{\text{N}(1)}|$ parameters again decrease in the $2\text{bz}'\text{py} \rightarrow 2\text{bzpy} \rightarrow 2\text{ppy}$ order: 104.7 ppm $\rightarrow$ 90.9 ppm $\rightarrow$ 77.0 ppm [12, 13]. The N(1) shielding is observed also for $[\text{Au}(2\text{apy}^*)\text{Cl}_2]$, being, however, ca. 10 ppm smaller than for $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$ (94.1 ppm versus 104.7 ppm).

The protonation of $2\text{bz}'\text{py}$ results in significant N(1) shielding as well, being ca. 13 ppm larger than for 2bzpy ($|\Delta_{\text{prot}}^{\text{N}(1)}|$: 111.1 ppm versus 97.9 ppm [13]; the change of solvent- CD_3CN versus $\text{DMSO}-d_6$ must be taken into account). This effect is typical for azines [36] and proves that $2\text{bz}'\text{pyH}^+$ cations remain stable in CD_3CN .

4. Conclusions

2-Acetylpyridine may coordinate Au(III) and Pd(II) central atoms in two different ways: by N(1), CH_2 -chelation of the deprotonated 2apy^* anion and by N(1), O-chelation of the neutral 2apy molecule. 2-Benzoylpyridine forms three various types of compounds with these metal ions: complexes with N(1)-monodentately bonded $2\text{bz}'\text{py}$ ligands, organometallics with the N(1), C(2')-cyclometallated $2\text{bz}'\text{py}^*$ anions, and salts containing protonated $2\text{bz}'\text{pyH}^+$ cations. Their ^1H , ^{13}C and ^{15}N NMR spectra reveal some interesting dependencies between the respective $\Delta_{\text{coord}}^{\text{H}}$, $\Delta_{\text{coord}}^{\text{C}}$, $\Delta_{\text{coord}}^{\text{N}}$ coordination shifts and the molecular structures. For $[\text{Au}(2\text{apy}^*)\text{Cl}_2]$ and $[\text{Au}(2\text{bz}'\text{py}^*)\text{Cl}_2]$ the most characteristic phenomenon is the large deshielding of the nitrogen-adjacent H(6) proton and the metallated CH_2 or C(2') carbons, as well as even more significant shielding of the coordinated N(1) nitrogen; the latter effect occurs also for $[\text{Au}(2\text{bz}'\text{py})\text{Cl}_3]$, $\text{trans}-[\text{Pd}(2\text{bz}'\text{py})_2\text{Cl}_2]$, and $2\text{bz}'\text{pyH}^+$.

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