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Preparation and NMR spectroscopic study of palladium(II) complexes with *N*-arylalkyliminodiacetamide derivatives

Neven Smrečki [a, *], Jarosław Jaźwiński [b, **], Zora Popović [a]

[a] *Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000, Zagreb, Croatia*

[b] *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, Warsaw, 01-224, Poland*

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ABSTRACT

The reactions of *N*-arylalkyl derivatives of iminodiacetamide, $RN(CH_2CONH_2)_2$; Rimda (Bnimda, Peimda, Ppimda, *o*-ClBnimda, *p*-ClBnimda; Bn = benzyl, Pe = 2-phenylethyl; Pp = 3-phenylprop-1-yl; *o*-ClBn = *o*-chlorobenzyl; *p*-ClBn = *p*-chlorobenzyl) with palladium(II) chloride in acidic aqueous solutions were investigated. Six new palladium(II) complexes, belonging to three different types, namely $[PdCl_2(Bnimda)]_2 \cdot 2H_2O$ (**1**; type **I**), $[PdCl_2(Peimda)] \cdot H_2O$ (**2**; type **II**), $[PdCl_2(Ppimda)] \cdot ½H_2O$ (**3a**; type **II**), $[PdCl_2(Ppimda)]_2$ (**3b**; type **I**), $[PdCl_2(p\text{-}ClBnimda)] \cdot H_2O$ (**4**; type **II**) and $[PdCl_2(o\text{-}ClBnimda)_2]$ (**5**; type **III**) were obtained and characterized by infrared spectroscopy, ^1H and ^{13}C NMR spectroscopy, and thermal analysis (TG/DTA).

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1. Introduction

Iminodiacetamide, $HN(CH_2CONH_2)_2$ (imda) is amide derivative of the iminodiacetic acid, $HN(CH_2COOH)_2$ ($idaH_2$) which is a well-known complexone [1]. Both chelators can act as tridentate ligands through their imino-nitrogen atoms and carbonyl (or carboxylate in the case of $idaH_2$) oxygen atoms. However, although structurally very similar to iminodiacetic acid, the coordination of iminodiacetamide predominantly depends on metal ion and counter-ions which are used for the reaction. Thus, imda can form cationic complexes of the type $[M(imda)_2]^{2+}$ (M = Cu(II) of Ni(II)) [2,3] or neutral ones like $[PdBr_2(imda)_2]$ [4]. Recently we have found that substitution of imino-hydrogen atom in the molecule of imda by an arylalkyl group (benzyl, substituted benzyl groups, 2-phenylethyl or 3-phenylprop-1-yl) leads to *N*-arylalkyliminodiacetamide derivatives which, interestingly, form stable complexes with Cu(II) and Ni(II), but not with Co(II) [5,6] and most probably some other metal ions. Palladium(II) and nickel(II) ions, although having analogous electron configurations (d^8), are characterized by completely different coordination chemistry [19]. Therefore, it is interesting to compare coordination environments around these two metal ions in Pd(II) and Ni(II) complexes with *N*-arylalkyliminodiacetamides [5,6].

Continuing our research on the chemistry of iminodiacetamide complexes, in this paper we present preparation and characterization of palladium(II) chloride complexes with afore mentioned *N*-arylalkyliminodiacetamide derivatives. Transition metal complexes with *N*-alkylated iminodiacetamides [2–8] and structurally related ligands [9–15] are generally scarce in the literature. To the best of our knowledge, there are no examples of an iminodiacetamide complex with any second- or third-row transition metal ion except $[PdBr_2(imda)_2]$ [4]. In order to get more insight into coordination chemistry of iminodiacetamide ligands and the role of the non-coordinating arylalkyl group in these systems, we have prepared six new palladium(II) complexes (Fig. 2) with *N*-arylalkyliminodiacetamides (Fig. 1) and characterized them by means of NMR spectroscopy, infrared spectroscopy and thermal analysis (TG/DTA).

2. Experimental

2.1. Materials and physical measurements

Palladium(II) chloride, containing 59% Pd by weight, was purchased from Alfa Aesar and used as received without further

* Corresponding author.
** Corresponding author.
E-mail addresses: nsmrecki@chem.pmf.hr (N. Smrečki), jaroslaw.jazwinski@icho.edu.pl (J. Jaźwiński).

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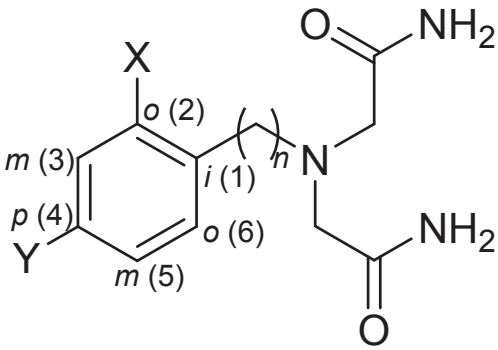

Fig. 1. Numbering scheme for ^{1}H and ^{13}C nuclei of the ligands and complexes. X = Y = H, *n* = 1 for Bnimda; X = Y = H, *n* = 2 for Peimda; X = Y = H, *n* = 3 for Ppimda; X = Cl, Y = H, *n* = 1 for *o*-ClBnimda; X = H, Y = Cl, *n* = 1 for *p*-ClBnimda. *i* = *ipso* (1), *o* = *ortho* (2, 6), *m* = *meta* (3,5), *p* = *para* (4).

purification. The ligands were prepared as reported earlier [5,6]. CHN analyses were performed on the Perkin-Elmer 2400 Series II CHNS analyzer in the Analytical Services Laboratories of the Ruđer Bošković Institute, Zagreb, Croatia. The IR spectra were obtained from KBr pellets in the range 4000–450 cm^{-1} with a Perkin-Elmer Spectrum RXI FTIR-spectrometer. TG/DTA measurements were performed at the heating rate of 10 °C min^{-1} in the temperature range of 25 and 600 °C, under nitrogen or oxygen flow of 180 mL min^{-1} on an instrument Mettler-Toledo TGA/SDTA 851e. Approximately 10 mg of sample were placed in a standard aluminium crucible (40 μL). All NMR measurements were performed on a Bruker DRX AVANCE 500 spectrometer equipped with a 5 mm triple broadband inverse probe (TBI) with a z-gradient coil. The measurements were carried out in DMSO-d_6 solutions, at the room temperature (303 K), using typical parameter values. Residual solvent signals were used as the secondary references, assuming 2.49 ppm (^{1}H) and 39.5 ppm (^{13}C) on the TMS signal (0 ppm). Typically, a set of ^{1}H NMR, ^{13}C NMR, and ^{1}H,^{13}C, g-HSQC and HMBC spectra was acquired.

2.2. Synthesis of the complexes

The ligand (2 mmol) was dissolved in 25 mL of water acidified with concentrated hydrochloric acid (5 drops), by gentle heating (≈50 °C). The obtained solution (pH ≈ 5) was treated with the solution of $PdCl_2$ (0.18 g; 1 mmol) in 25 mL of water (also acidified with 5 drops of hydrochloric acid and heated to ≈ 50 °C). The resulting reaction mixtures were left to stand at room temperature. The obtained complexes were filtered off, washed with water (10 mL) and dried in air. The complexes are soluble in dimethyl sulfoxide and *N*,*N*-dimethylformamide but almost insoluble in water.

2.2.1. [$PdCl_2$(Bnimda)]$_2$ · 2H_2O (**1**)

From 0.48 g Bnimda · H_2O. The brown microcrystalline product obtained after spontaneous evaporation of the resulting orange-brown solution (pH ≈ 1) for one week at room temperature. The product was filtered off and washed with water (10 mL). *Anal.* Calc. for $C_{11}H_{17}N_3O_3Cl_2Pd$ (416.56): C 31.72, H 4.11, N 10.09%. Found: C 31.46, H 3.88, N 9.89%. The assigned IR data (cm^{-1}): 3318(s) and 3186(s) (ν_{as} and ν_s of NH_2), 1662 (vs) (ν(C=O)). Other IR data (cm^{-1}): 3380(s), 1602(m), 1560(m), 1492(w), 1454(m), 1412(w), 1320(w), 1302(w), 1256(w), 1212(w), 1152(w), 1112(w), 1084(w), 1048(w), 1014(w), 960(w), 940(w), 910(w), 884(w), 866(w), 816(w), 760(m), 707(w), 616(w), 528(w).

^{1}H NMR (ppm), $^{gem}J(H,H)$ (*Hz*), [^{13}C NMR] (ppm):
3.43d^{a} (1H), 3.82d (1H), *J 16.4*, [62.5] CH_2, [178.4] C=O (heterocyclic ring);
3.43d^{a} (1H), 4.01d (1H), *J 15.5*, [60.9] CH_2, [168.7] C=O, 7.26 (1H), 7.60 (1H), CONH_2 (amide branch);
4.00d (1H), 4.27d (1H), *J 12.8*, [64.9] CH_2Ph, 7.47 m, [128.4, 128.9] Ph(*m*, *p*), 7.93d (2H) [132.2] Ph(*o*), [133.2] Ph(*i*) (Ar branch).
Signals not assigned: 4.04 vbr [58.1 vbr], [55.5 vbr], 7.42 m (18H), [128.5], [130.1 vbr].
^{a}signals (doublets) overlapped

2.2.2. [$PdCl_2$(Peimda)] · H_2O (**2**)

From 0.50 g Peimda · H_2O. Yellow powder started to precipitate after mixing the solutions of the reactants. The obtained suspension was stirred, left to stand for 2 h, filtered and washed. Yield: 0.19 g (44%). *Anal.* Calc. for $C_{12}H_{19}N_3O_3Cl_2Pd$ (430.59): C 33.47, H 4.45, N 9.76%. Found: C 33.66, H 4.57, N 9.90%.

The assigned IR data (cm^{-1}): 3319(s) and 3188(m) (ν_{as} and ν_s of NH_2), 1680(vs) and 1584(vs) (ν(C=O)). Other IR data (cm^{-1}): 3522(m, sh), 3400(m), 3025(w), 1495(w), 1454(w), 1410(w), 1387(w),1339(w), 1245(w), 1116(w), 1085(w), 1067(w), 1030(w), 990(w), 953(w), 924(w), 880(w), 822(w), 750(w), 703(m), 669(w), 600(w).

^{1}H NMR (ppm), $^{gem}J(H,H)$ (Hz), [^{13}C NMR] (ppm):
3.47d (1H), 3.86d (1H), *J = 17.5*, [63.2]^{a} CH_2, [179.2] C=O (heterocyclic ring);
3.51d (1H), 3.94d (1H), *J = 15.5*, [61.4] CH_2, 7.26 NH (1H), 7.60 NH (1H), CONH_2, [168.5] C=O (amide branch);
3.03 m, 3.18 m, [63.2]^{a} CH_2CH_2Ph, 3.17 m, 3.90m^{b} [34.3] CH_2Ph,
Signals not assigned:
2.70 m, [56.6], 2.75 m [56.6], 3.14br, [56.6], 3.33vbr, 3.38s [55.0], 7.30 m (Ph) [125.9], [126.5], [128.2], [128.5], [128.6], [128.8], [138.0] Ph, [171.4] C=O.
^{a}two signals with similar chemical shifts, $\Delta\delta$ 0.03 ppm, ^{b}the signal overlapped with the signals at 3.86 and 3.94 ppm.

2.2.3. [$PdCl_2$(Ppimda)] · ½H_2O (**3a**)

From 0.50 g Ppimda. Yellow powder started to precipitate immediately. The reaction mixture was stirred for 5 min and left to stand for 2 h. The product was filtered off and washed with water (10 mL). Yield: 0.15 g (36%). *Anal.* Calc. for $C_{13}H_{20}N_3O_{2.5}Cl_2Pd$ (435.61): C 35.84, H 4.63, N 9.65%. Found: C 35.30, H 4.91, N 10.10%.

The assigned IR data (cm^{-1}): 3317(m) and 3183(m) (ν_{as} and ν_s of NH_2), 1680(vs) and 1577(vs) (ν(C=O)). Other IR data (cm^{-1}): 3404(m, br), 3024(w), 2933(w), 2860(w), 1495(w), 1452(m), 1413(w), 1318(w), 1251(w), 1118(w), 1017(w), 955(w), 917(w), 887(w), 850(w), 808(w), 754(w), 701(m).

^{1}H NMR (ppm), $^{gem}J(H,H)$ (Hz), [^{13}C NMR] (ppm):
3.18d (1H), 3.82d (1H), *J = 16.6*, [63.7] CH_2, [179.1] C=O (heterocyclic ring);
3.35d (1H), 3.85d (H), *J = 15.8*, [61.2] CH_2, [168.7] C=O (amide branch);
2.18 m, 2.80m^{a}, [29.5] $CH_2CH_2CH_2$Ar, 2.71 m (2H), [32.5]^{b} $CH_2CH_2CH_2$Ar, 2.82m^{a}, 2.99 m, [61.8] $CH_2CH_2CH_2$Ar.
Signals not identified:
1.82vbr, 2.59 m [32.0br] 3.31br, 3.91br
^{a}signals overlapped; ^{b}probably two signals overlapped

2.2.4. [$PdCl_2$(Ppimda)]$_2$ (**3b**)

From 0.50 g Ppimda. After few days of standing at room

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