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Complexes of Palladium(II) with Adenosine

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The coordination of nucleosides and their constituent bases to palladium has been subject of recent articles [1–4]. Adenosine has been shown to bind to diethylenetriaminepalladium(II) in aqueous solution through N-1 or N-7 of the purine base and through both N-1 and N-7 sites simultaneously [1]. We report here the isolation and characterization of palladium(II)–adenosine complexes of the type [Pd(Adenosine)X_2] and [Pd(Adenosine)$_2X_2$]·2DMSO (X = Cl, Br).

The complexes [Pd(Adenosine)X_2] separate from equimolar solutions of Na_2PdX_4 and adenosine in water. The complexes [Pd(Adenosine)$_2X_2$]·2DMSO slowly separate from concentrated DMSO solutions of [Pd(DMSO)$_2X_2$] and adenosine in the molar ratio 1:2. Satisfactory elemental analyses were obtained in all the cases. The compounds are weak electrolytes in DMSO. Molar conductivities in the range 1–2 S cm^2 mol^{-1} were measured (10^{-3}–10^{-2} *M* solutions), whereas values in the range 23–42 are characteristic for 10^{-3} *M* solutions of 1:1 electrolytes in this solvent [5].

A structure of the complexes [Pd(Adenosine)$_2$-X_2]·2DMSO involving two monodentate adenosine ligands and two halide ions in the first metal coordination sphere can be deduced from the behaviour of DMSO solutions (conductivity and NMR) and stereochemical properties of palladium(II). The presence of metal-bonded halides in the solid compounds is confirmed by shift to lower frequency of the absorption in the 25 kK region on going from X = Cl to Br. (Nujol mulls).

The IR spectra of the complexes [Pd(Adenosine)-X_2] in Nujol display a weak, broad band at 355 cm^{-1} (X = Cl) and 255 cm^{-1} (X = Br), respectively, assigned to the Pd–X stretch. These values are consistent with the presence of two terminal halide ligands, although their relative arrangement cannot be decided. Two possible structures could be suggested for the [Pd(Adenosine)X_2] adducts, based on four coordination of palladium(II): (1) a chelate complex involving the NH_2 group and either the N-1 or the N-7 atom; (2) a polymeric structure, similar to that found for the compound $AgNO_3$–9-methyladenine·H_2O [6], where each adenosine ligand bridges two PdX_2 moieties through its N-1 and N-7 atoms. The presence of the second structure can be inferred from NMR observations on the systems [Pd(DMSO)$_2X_2$]–adenosine in solution. It is pertinent to note that metal complexation of purine bases through N-3 is known to occur only when the N-9 position is exposed and the purine acts as a bidentate ligand *via* both N-3 and N-9 [7].

The ^1H NMR spectra of the complexes [Pd(Adenosine)X_2] and [Pd(Adenosine)$_2X_2$]·2DMSO in DMSO-d_6 are similar to those measured for solutions of [Pd(DMSO)$_2X_2$] and adenosine in the appropriate molar ratio. Chemical shift data of the purine protons are quoted in Table I. Spectra of mixtures of [Pd(DMSO)$_2X_2$] and 8-deuterioadenosine have also been measured in order to assign H-2 and H-8 resonances. Some spectra of solutions containing 3 to 5 *M* H_2O or D_2O have been recorded for analysis of exchangeable protons. The addition of water appear to have no important effects upon intensities and chemical shifts of H-2 and H-8 signals.

TABLE I. Chemical Shifts of Adenosine Protons (ppm downfield from TMS).

	H-2	NH_2	H-8
Adenosine	8.16	7.34	8.36
[Pd(Adenosine)$_2Cl_2$]·2DMSO	9.10	8.78	8.50
[Pd(Adenosine)$_2Br_2$]·2DMSO	9.16	8.76	8.50
[Pd(Adenosine)Cl_2]	9.12	8.79	8.52
	8.36	8.56	
[Pd(Adenosine)Br_2]	9.18	8.79	8.53
	8.37	8.56	
[Pd(DMSO)$_2Cl_2$]–Adenosine 5:1	8.53	8.8	8.93
[Pd(DMSO)$_2Br_2$]–Adenosine 5:1	8.52	8.8	8.86

In the complexes [Pd(Adenosine)$_2X_2$] both H-2 and H-8 signals are shifted downfield with respect to free adenosine, but the shift of the H-2 proton is much greater and is consistent with binding of adenosine to palladium(II) through the N-1 atom. The NMR data of these complexes must be compared with data of analogous platinum(II) derivatives [8]. The complex [Pt(Adenosine)$_2Cl_2$], where binding of adenosine through N-7 occurs, displays resonances at δ = 8.46 (H-2) and 9.33 (H-8) in DMSO-d_6 solution. Although the effects of possibly different configurations (*cis* or *trans*) at the metal center should be taken into account, there seems to be little doubt that the reversal in the order of H-2 and H-8 proton signals is related to a different binding mode of adenosine in the palladium and platinum complexes. Partial dissociation of the adducts [Pd(Adenosine)$_2$-X_2] in DMSO occurs; presence of 10–20% free adenosine is apparent in 0.1 *M* solutions.

TABLE II. Adenosine ^{13}C Chemical Shifts (ppm downfield from TMS).

	C-2	C-4	C-5	C-6	C-8
Adenosine[a]	152.6	149.3	119.6	156.3	140.2
Adenosine 0.48 *M* –H_2SO_4 0.24 *M*	148.6	148.6	118.9	152.8	141.2
$[Pd(DMSO)_2Cl_2]$ 0.2 *M* –Adenosine 0.2 *M*	152.6	147.1	118.7	154.2	141.2

[a] Data from reference 9.

Solution of the compounds $[Pd(Adenosine)X_2]$ in DMSO reasonably implies cleavage of the proposed polymeric structure and partial substitution of metal–adenosine by metal–DMSO bonds. The NMR behaviour of these adducts and of equimolar mixtures of $[Pd(DMSO)_2X_2]$ and adenosine is complex, indicating the presence of several species. However, by addition of an appropriate excess of $[Pd(DMSO)_2X_2]$ the spectrum is simplified. The species appearing at a palladium to adenosine ratio of 5 (see Table I) can be identified as a complex with two metal atoms bridged by a nucleoside molecule through N-1 and N-7. The spectra of equimolar mixtures of palladium and adenosine (or 8-deuterioadenosine) show two main sets of H-2 and NH_2 resonances (see Table I). The corresponding H-8 signals are not resolved, but instead a single rather broad peak is observed. Free adenosine is not present at appreciable concentration. Other minor resonances are also apparent; in the spectrum of mixtures with 8-deuterioadenosine a signal at $\delta = 8.5$ can be ascribed to bridging adenosine. Concentration dependence of the spectra is observed. For example, the ratio of peak height of the lowfield with respect to the high field H-2 resonance is decreased with decreasing concentration (0.2–0.01 *M*). A similar effect is produced by addition of an excess of $[Pd(DMSO)_2X_2]$. These results can be tentatively accounted for by coordination equilibria involving a complex with two adenosine molecules bonded through N-1 (lowfield H-2 resonance), a complex containing a single adenosine molecule bonded through either N-1 or N-7 (high field H-2 resonance), and a binuclear complex with bridging adenosine.

It must be noted that in all the cases the NMR behaviour of corresponding chloro- and bromo derivatives is similar. Moreover, in solutions with palladium to adenosine ratio of 1:2 and 1:1.5 no significant shift of aromatic and NH_2 resonances of free adenosine is produced by the presence of palladium adducts. The above observations rule out significant halide–nucleoside interactions through hydrogen bonds in these systems.

The ^{13}C NMR spectrum of a solution of 0.2 *M* $[Pd(DMSO)_2Cl_2]$ and 0.2 *M* adenosine has been measured. The main set of signals observed is assigned to N-1 bonded adenosine. Data for purine carbons are quoted in Table II. Ribose resonances are measured at $\delta_C = 87.9$ (C-1′), 73.8 (C-2′), 70.2 (C-3′), 85.8 (C-4′), and 61.2 (C-5′). Comparison with spectra of free and protonated adenosine (see Table II) shows that the changes of chemical shift observed upon complexation for all purine carbons but C-2 parallel the changes observed upon protonation of asenosine. Lack of upfield shift for C-2 upon complexation through N-1 is observed also in the case of the $[Pd(diethylenetriamine)(OH_2)]^{2+}$–adenosine system [1]. Similar values of ^{13}C chemical shift are reported for adenosine complexed to mercury(II) [10].

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