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T13

Palladium Compounds of Xanthine and Xanthine Derivatives

E. COLACIO, J. M. SALAS, M. A. ROMERO, A. SÁNCHEZ and M. NOGUERAS

Department of Inorganic Chemistry, Faculty of Sciences, Granada University, Spain

The biological importance of purine bases is well known. The interaction of metal ions with nucleic acids, nucleosides and nucleotides has been an active area of inorganic and structural chemistry during the last few years, and a number of recent reviews exist on the subject [1, 2]. Recently much attention has been paid to palladium-containing complexes, due to their potent anti-tumor activities [3–7]. We report here the synthesis and characterisation of Pd(II) complexes with xanthine (XH), theophylline (TH), theobromine (TBH), 3,8-dimethylxanthine (DMH), caffeine (C) and 1,3,8-trimethylxanthine (TMH).

Experimental

The chemicals theophylline, theobromine, caffeine and $PdCl_2$ were purchased from Carlo Erba; and were used without further purification. 3,8-dimethylxanthine and 1,3,8-trimethylxanthine were synthesized in our laboratory [8, 9]. The Pd(II) complexes of these ligands were prepared in acid media (HCl 0.25 *N*), mixing solutions of the ligands and metal salt, $PdCl_2$ (2:1 mole ratio). Tetrachloro palladates were obtained from solutions with ligand: cation relation equal to 1:1 in acid media (HCl 2.5 *N*). The precipitates formed in each case were washed with distilled water, ethanol and ether and then air-dried.

The IR spectra were run on Beckman 4250. ^1H NMR studies were performed in DMSO-d_6 on Hitachi Perkin Elmer R-600 high resolution NMR spectrometer. TMS was used as internal reference.

Results and Discussion

Table I gives the colour, elemental analysis and the position of the stretching bands Pd–Cl and Pd–N of the isolated complexes.

TABLE I. Colour, Elemental Analysis and ν(Pd–Cl) and (Pd–N)[a] (cm^{-1}).

Compound	Colour	C	H	N	Cl	Pd	ν(Pd–Cl)	ν(Pd–N)
$[XH_2]_2[PdCl_4]\cdot 2H_2O$	brown	20.32	2.37	18.97	24.05	18.02	310	
		21.19	2.42	18.74	23.87	17.52		
$Pd(XH)_2Cl_2\cdot 2H_2O$	yellow	23.27	2.31	21.72	13.77	20.63	350	260
		22.90	2.03	21.41	13.85	19.72		
$[TH_2]_2[PdCl_4]$	brown	27.52	2.95	18.35	23.26	17.43	330	
		27.68	2.98	18.53	23.10	16.80		
$Pd(TH)_2Cl_2$	yellow	31.26	2.98	20.84	13.21	19.80	340	250
		31.40	2.84	20.88	13.52	19.20		
$[TBH_2]_2[PdCl_4]$	brown	27.52	2.95	18.35	23.26	17.43	305	
		27.39	3.01	18.64	23.35	17.26		
$Pd(TBH)_2Cl_2$	yellow	31.26	2.98	20.84	13.21	19.80	345	255
		30.78	3.01	20.69	13.52	19.40		
$Pd(DMH)_2Cl_2$	yellow	31.26	2.98	20.84	13.21	19.80	340	250
		30.28	2.89	20.27	12.80	19.80		
$Pd(C)_2Cl_2$	yellow	33.95	3.54	19.81	12.56	18.82	340	260
		33.92	3.42	19.60	13.05	18.71		
$Pt(TMH)_2Cl_2$	yellow	31.92	3.99	18.62	11.80	17.70	335	250
		32.34	3.96	18.17	11.70	18.20		

[a] Calculated values of elemental analysis in first row.

TABLE II. ^1H NMR Chemical Shifts in ppm.

Proton	XH	$Pd(XH)_2Cl_2$	TH	$Pd(TH)_2Cl_2$	TBH	$Pd(TBH)_2Cl_2$
C-8-H	7.90	8.30	7.95	8.05	7.97	7.97
C-8-CH_3						
Proton	DMH	$Pd(DMH)_2Cl_2$	C	$Pd(C)_2Cl_2$	TMH	$Pd(TMH)_2Cl_2$
C-8-H			7.95	7.95	2.40	2.40
C-8-CH_3	2.35	2.70				

From magnetic data, (all the compounds are diamagnetic) square planar structures for PdL_2Cl_2 complexes (where L = XH, TH, TBH, DMH, C and TMH) and tetrachloro palladate anion have been proposed.

In PdL_2Cl_2 complexes complexation of the purine base to Pd(II) causes downfield shifts of protons adjacent to the coordination site. Table II shows the proton chemical shifts in parts per million of the ligand and its Pd(II) complexes. The shift to downfields experienced by C-8-H and C-8-CH_3 protons is indicative of complexation at the N_9 position of the ligand (except for the xanthine).

The infrared spectra of PdL_2Cl_2 complexes showed single Pd–Cl and Pd–N stretching bands. This is consistent with a *trans*-configuration. In the tetrachloro palladate compound only the ν(Pd–Cl) is present.

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T14

Crystal Structure of the $[Pt(9\text{-Methylguanine})_4]^{2+}$ Cation

HANS-JÜRGEN KORTE and ROBERT BAU

Department of Chemistry, University of Southern California, Los Angeles, Calif. 90089, U.S.A.

The $[Pt(9\text{-methyl-guanine})_4]^{2+}$ cation is the first example of a Pt^{2+} compound to have four purine bases as ligands. This compound is especially interesting as it was suggested earlier that the anti-tumor drug *cis*-dichlorodiammineplatinum(II) could lose all four ligands in order to interact with the purine bases of the DNA double helix [1].

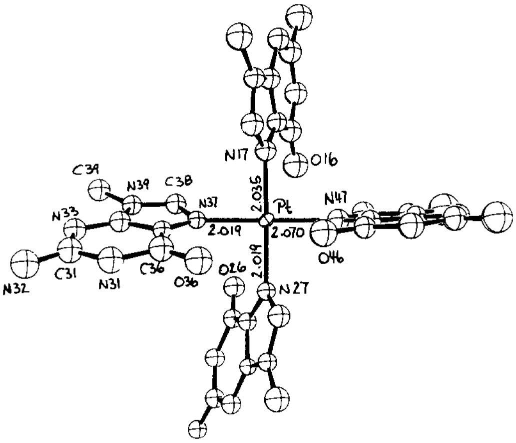

Fig. 1. Structure of the complex.

The title compound was prepared by heating K_2PtCl_4 with excess 9-methylguanine (ratio 1:6) under reflux for several hours. The reaction mixture was separated by preparative reverse-phase high-performance liquid chromatography to remove excess ligand and some minor impurities possibly due to the formation of other Pt–guanine complexes. $[Pt(9\text{-Methylguanine})_4]^{2+}Cl^-(CF_3COOH)^-$ crystallizes as colorless bricks in the triclinic space group $P\bar{1}$, with $a = 16.234(8)$ Å, $b = 13.475(7)$ Å, $c = 10.856(5)$ Å, $\alpha = 103.80(4)°$, $\beta = 91.40(4)°$, $\gamma = 115.50(3)°$, $Z = 2$. The structure consists of a $Pt(9\text{-MeG})_4^{2+}$ cation in which each purine ligand is coordinated through its N(7) nitrogen atom (Fig. 1) to result in a PtN_4-square plane. The purine ligands are in the usual alternating head to tail arrangement with the adjacent C(6)–O(6) pointing in opposite directions. The average Pt–N distance is 2.036 Å. The current R-value is 7.8% with 4475 independent reflections.