

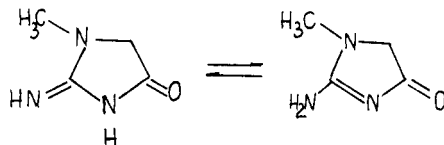
New platinum(II) and platinum(III) complexes of creatinine

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Abstract - The interaction of Pt(II) with creatinine is studied in different reaction conditions. At L:M ratio from 4 to 10 several new complexes of Pt(II) are obtained, studied by spectroscopic methods and X-ray diffraction. In these monomeric species the ligand is coordinated only through the endogenous nitrogen. At L:M = 1 a slow redox process takes place leading to the formation of several (neutral, anionic and cationic) blue to green paramagnetic species. The process proceeds on with a marked decrease of pH and is sensitive to the acidity, to the nature of the solvent (H₂O, D₂O or organic solvent) and to the presence of O₂ as well. A green monomeric species was isolated and studied by X-ray structural analysis.

1 INTRODUCTION

Creatinine (Creat), being a natural metabolite of creatine, is an important bioligand. The presence of several donor groups in its main tautomeric forms determines its strong coordination capacity. Recently its complexation



ability towards a number of metal ions: Ag(I), Hg(II), Cd(II), Zn(II), Co(II), Ni(II), Cu(II), Pt(II), Pd(II) was studied (ref. 1-11). The experimental data obtained up to now by us and other authors show that the complexation ability of the ligand and the type of the complexes formed strongly depend on the reaction conditions. That was confirmed, for example, in the case of Cu(II) (ref. 2,6) and Pt(II) complexes (ref. 7,8,10,11) obtained from water solutions. Recently we have shown that Ni(II) - creatinine complexes are formed only in nonaqueous medium (ref. 9).

On the other hand in the course of Pt(II) - creatinine interaction redox processes take place too, resulting in formation of paramagnetic species of the type of "Platinum Blues" (ref. 7,8).

Numerous experimental data are available in the literature, showing on the strong influence of the reaction medium both on complex formation (ref. 12) and redox reactions with metal complexes (ref. 13) and especially on stabilization of intermediate oxidation states - Cr(V), Cu(I) etc. (ref. 14-16). It might be expected therefore formation and stabilization of Pt(III) to be dependent both on the reagents and on the reaction conditions, here including the reaction medium on a first place.

In the present paper results concerning the formation of different Pt(II) and Pt(III) complexes of creatinine obtained at different conditions are reported.

2 SYNTHESIS AND STRUCTURE OF MONOMERIC Pt(II) COMPLEXES

Complexes Pt(II) - creatinine are formed as a result of Pt(II) interaction with creatinine at ligand excess (L:M = 4:1) (ref. 7,9,10). Two types of complexes were obtained: charged $\text{Pt}(\text{Creat})_4^{2+}$ and neutral $\text{cis-Pt}(\text{Creat})_2(\text{NO}_2)_2$, depending on the starting Pt(II) species.

2.1 Complexation between PtCl_4^{2-} and creatinine

At ligand excess (L:M = 4) creatinine and PtCl_4^{2-} form a positively charged complex, isolated from the solution by precipitation with a large anions A^- such as ClO_4^- or tetraphenylborate (TPB). The analytical data have shown on the formation of $\text{Pt}(\text{Creat})_4\text{A}_2$.

X-ray diffraction analysis of $\text{Pt}(\text{Creat})_4(\text{ClO}_4)_2$ (monoclinic crystal system, space group C2/c) was performed (ref. 10). The ligand participates in the complex in its amino form, the coordination being realized only through the endocyclic nitrogen. A square planar coordination in respect of the four nitrogens (Pt—N distance 2.00 Å) is realized, the ligand planes being almost perpendicular to the PtN_4 - plane. The tilting angles range from 82.1(8) to 93.5(9)° due to both intramolecular steric factors and intermolecular H-bond formation between the amino-hydrogen atoms and the oxygens from ClO_4^- . The perchlorate ions are surrounded by four creatinine ligands, parallel in pairs (coordinated to two different Pt(II) and rotationally disordered). The packing of the molecules within the unit cell as well as detailed description of the structure are in press (ref. 10).

In contrast to diperchlorate complex salt, $\text{Pt}(\text{Creat})_4(\text{TPB})_2$ is an "amorphous" substance. The similarity in their IR spectra indicates on similarity in the mode of coordination in both complex salts. The IR data obtained (Table 1) provide information for the H-bonding in them. In $\text{Pt}(\text{Creat})_4(\text{TPB})_2$ only one type of H-bond is realized, namely between NH_2 and C=O groups, while in $\text{Pt}(\text{Creat})_4(\text{ClO}_4)_2$ the additional network of H-bonds between NH_2 and ClO_4^- leads to the appearance of two couples of bands for the NH_2 stretching (symmetric and asymmetric) vibrations and two bands for the NH_2 bending vibrations (ref. 17). Evidently the H-bond formation is responsible for the crystalline structure of $\text{Pt}(\text{Creat})_4(\text{ClO}_4)_2$ in contrast to $\text{Pt}(\text{Creat})_4(\text{TPB})_2$.

TABLE 1. Selected IR data for the Pt(II) complexes

Compound	ν_{NH_2}	δ_{NH_2}	$\nu_{\text{C=O}}$	ν_{NO_2}	δ_{ONO}	$\nu_{\text{Pt-NO}_2}$	$\nu_{\text{Pt-N(endo)}}$
Creat	3254 3040	1660	1685	-	-	-	-
$\text{Pt}(\text{Creat})_4(\text{TPB})_2$	3390 3330	1665	1705	-	-	-	-
$\text{Pt}(\text{Creat})_4(\text{ClO}_4)_2$	3410 3315 3290 3215	1675 1655	1725	-	-	-	-
$\text{Pt}(\text{NO}_2)_4^{2-}$	-	-	-	1466 1397 1343	847 839 833	421	-
$\text{Pt}(\text{Creat})_2(\text{NO}_2)_2$	3393 3280 3343 3223 3280sh 3171	1666	1745sh 1721	1530sh 1376 1520 1358 1503 1328	858 841	491 br	326

It should be mentioned that analogous elemental and IR spectral data were obtained for the corresponding $\text{Pd}(\text{Creat})_4^{2+}$ complexes too (ref. 10).

2.2 Complexation between $\text{Pt}(\text{NO}_2)_4^{2-}$ and creatinine

Using $\text{Pt}(\text{NO}_2)_4^{2-}$ as a starting Pt(II) compound neutral, low soluble complex $\text{cis-Pt}(\text{Creat})_2(\text{NO}_2)_2$ was synthesized as a crystalline powder of monoclinic crystal system, space group $\text{P2}_1/\text{n}$. The structure of the complex as well as the packing in the unit cell are already described in detail (ref. 11).

In this case creatinine again acts as monodentate ligand, present in its amino form and coordinated through the endocyclic N-atom. Square-planar PtN_4 coordination of two cis-disposed NO_2^- groups ($\text{Pt}-\text{N}_{\text{av}}$ 2.023(7) Å) and two creatinine molecules ($\text{Pt}-\text{N}_{\text{endo,av}}$ 1.991(8) Å) is realized. The creatinine rings are planar and tilted to the equatorial plane by 80° . Studying the packing of molecules in the unit cell it was established that several types of H-bonds are formed (including NH_2 , $\text{C}=\text{O}$ and NO_2^-) thus stabilizing the structure by a three-dimensional network of H-bonds. The IR data obtained are in agreement with these results (Table 1). The formation of this network is most probably responsible not only for the crystal structure of the complex but for its low solubility as well.

The analysis of H-bonds formed indicates on unusual function of the amino group. It acts as a normal H-bond donor through one of its H-atoms in an intramolecular H-bond with the carbonyl oxygen, and through the second H-atom - in an intermolecular H-bond with oxygen from NO_2^- . In the same time the nitrogen of the NH_2 group serves as H-atom acceptor in its interaction with another NH_2 .

The crystallographic data show on difference between $\text{N}-\text{O}$ distances in the NO_2^- groups ($\text{N}-\text{O}$ 1.24(1) Å, while $\text{N}'-\text{O}'$ 1.21(1) Å), together with change in their tilting to the PtN_4 -plane ($83.1^\circ/41.6^\circ$). These differences are most probably due to the non-equal participation in the H-bond network realized in the crystal structure.

3 Pt(III) FORMATION AND STABILIZATION DURING Pt(II)-CREATININE INTERACTION

By means of EPR spectroscopy it was found that in the course of Pt(II)-creatinine interaction paramagnetic species are formed giving rise of a broad singlet ($g = 2.52 \pm 0.01$ at 77K), assigned to Pt(III) species. At ligand excess, however, these species are not stabilized and the reaction results in $\text{Pt}(\text{Creat})_4^{2+}$ formation as described above. In order to study the formation of Pt(III) and the possibilities for its stabilization the reaction was studied at lower L:M ratios. At L:M = 1:1 a blue colour developed several hours after mixing the reagents (new bands at 560, 680, 750, 1200 and 1500 nm were observed in the spectrum). The reaction mixture thus obtained exhibits anisotropic EPR spectrum ($g_{\perp} = 2.54$, $g_{\parallel} = 1.98$ at 77K). These data are similar to those of other paramagnetic "Platinum Blue" complexes (ref. 18). Polarographic and ESCA measurements were performed too. Both the values of binding energies for Pt 4f_{7/2} 73.5(2) and 74.6(2) eV and half-wave potentials 180 and 380 mV (Pt working electrode and SCE as a reference) are typical for mixed Pt(II)/Pt(III) complexes of "Platinum Blue" type (ref. 19,20).

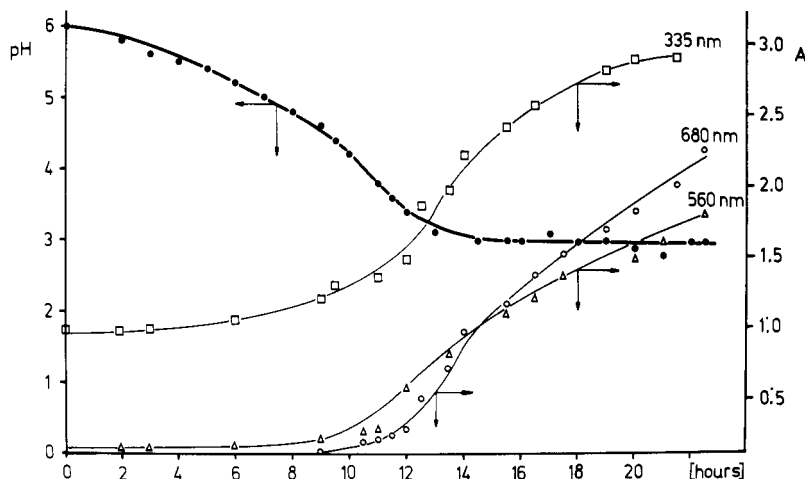


Fig. 1. Time dependence of pH and absorbance of the system PtCl_4^{2-} -Creat (L:M = 1:1)

Several days after mixing the reagents (L:M = 1:1) the EPR spectrum of the system indicates on the existence of at least three paramagnetic species. In the same time a blue paramagnetic precipitate is formed spontaneously in the reaction course. Adding large anions (AsF_6^- or PF_6^-) and cations (AsPh_4^+ or PPh_4^+) to the reaction mixture, positively and negatively charged paramagnetic platinum complexes were isolated respectively. The formation of at least three oligomer complex species was also confirmed by means of HPLC (gel filtration).

The PtCl_4^{2-} -creatinine interaction at molar ratio 1:1 was followed spectrophotometrically at 335, 560 and 680 nm where the absorption bands of the initial PtCl_4^{2-} and the complex species formed are located. The acidity of the solution in the reaction course was monitored too. The results obtained are represented on Fig. 1.

It can be seen that the formation of "Platinum Blue" complexes is connected with significant decrease of pH, changing from pH 6 at the beginning to pH 3 at the end of the reaction. In the same time the kinetic data show that the new absorption bands increase their intensity most of all after the change in the acidity. The substitution of water as reaction medium with D_2O leads to a marked decrease of the reaction rate (Fig. 2). The kinetic isotopic effect might be connected either with N—H bond cleavage or with participation of water in the rate-limiting step of the process studied.

It must be emphasized that in the absence of oxygen (in argon atmosphere) the reaction rate decreases several times and a change of the reaction products is observed.

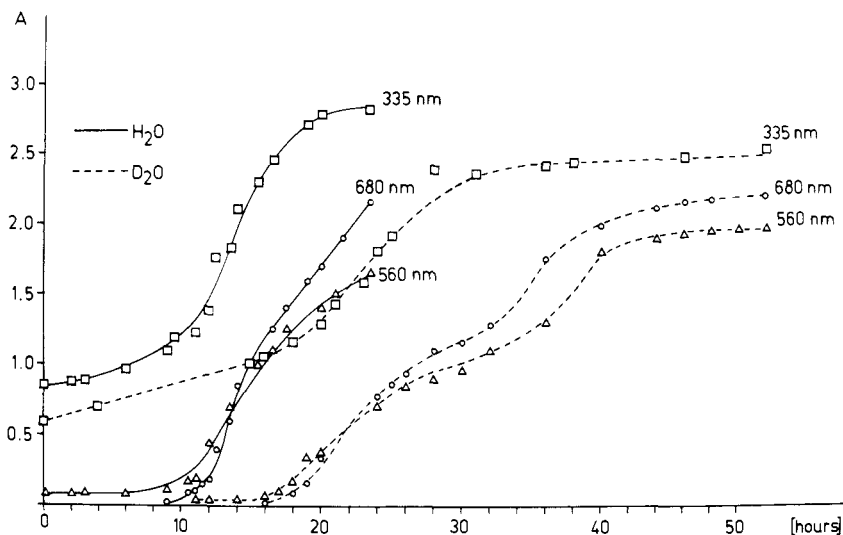


Fig. 2. Kinetic isotopic effect. Time dependence of absorbance of the system PtCl_4^{2-} -Creat (L:M = 1:1) in H_2O and D_2O

In order to study the influence of the acidity on the reaction, it was performed at different initial pH-values, adjusted by addition of KOH or HClO_4 . It was found that depending on the acidity different species are obtained. The results are summarized in Table 2, where the pH-values at the beginning and the end of the reaction are shown.

TABLE 2. Products obtained at different pH-values

pH-values		Absorption bands (nm)	Remark
initial	final		
10.0	7.0	520	KOH added
~6	~3	560, 680	no additions
4.2	3.5	680, 740	KOH added in the reaction course
3.0	2.3	680, 740	
2.9	2.4	680	EPR $\epsilon_{\perp} > \epsilon_{\parallel}$
2.2	1.5	680	EPR $\epsilon_{\parallel} > \epsilon_{\perp}$
0.9	0.5	390	

In the pH-range 10.0 - 7.0 the reaction proceeds slowly with the formation of violet paramagnetic species. In acidic media it goes on faster with different "Platinum Blues" as final products. Thus at lower pH-values two green paramagnetic complexes are formed. The one, isolated at pH 2.4 shows a multiplet EPR signal with $g_{\perp} > g_{\parallel}$, while for that, obtained in more acidic medium (pH 1.5) the reverse position $g_{\parallel} > g_{\perp}$ was obtained. In stronger acidic solution (pH 0.3-0.9) only diamagnetic yellow complex is formed. It must be emphasized that when buffer solutions with pH 8.0 (ammonia) and 7.2 (HEPES) were used, no reaction takes place at all in the system.

If the reaction is carried out without any acidity corrections in the system (initial pH ~ 6, final pH ~ 3) several blue compounds are formed in the solution, separated by means of reverse phase HPLC. These include neutral species precipitated spontaneously after several days, positively charged, precipitated by AsF_6^- or PF_6^- and negatively charged, separated with AsPh_4^+ or PPh_4^+ . The EPR spectrum of the negatively charged complex, precipitated by AsPh_4^+ indicates that the complex is an oligomer with more than four platinum atoms in the chain, their number being most probably six (Fig. 3).

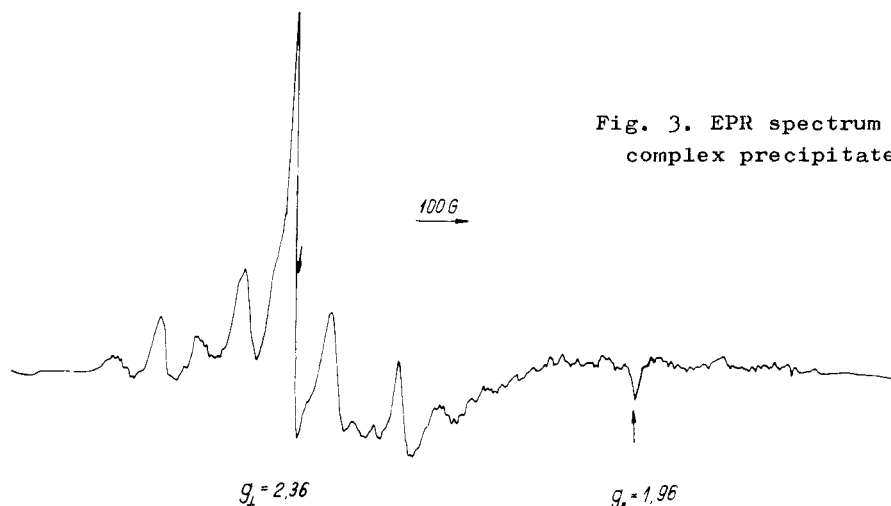


Fig. 3. EPR spectrum of the blue complex precipitated by AsPh_4^+

After the addition of the large cation AsPh_4^+ and the filtration of the blue precipitate, the pH-value is about 2.4. After one day in this solution green paramagnetic crystals are formed. The structure of this complex was studied using X-ray diffraction analysis. The preliminary data obtained show on the formation of monomeric complex (monoclinic crystal system, space group $P2_1$), containing one creatinine molecule, three chloride ions and one counter ion (Fig. 4). More precise structural, EPR, magnetochemical and electrochemical data for this monomeric and the other oligomeric species obtained will be published soon (ref. 21).

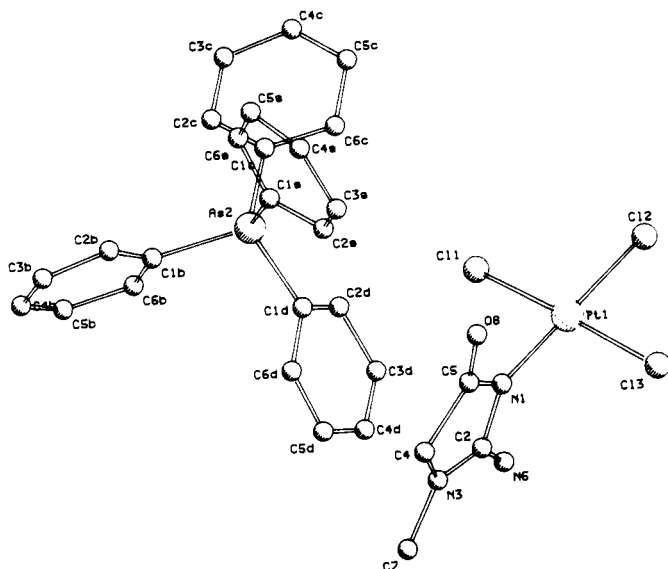


Fig. 4. ORTEP drawing of $[\text{Pt}(\text{Creat})\text{Cl}_3](\text{AsPh}_4)$

In order to check the assumption for water participation in the reaction course, the PtCl_4^{2-} -creatinine reaction was studied in nonaqueous media: in acetonitrile (An), absolute methanol, ethanol, methylacetamide (MAA), HMPA, DMF and DMSO. Studying the electronic spectra of the reaction system it was established that in anhydrous solvents no interaction took place between the reagents. In the presence of small amounts of water, however, redox and complexation processes occurred, resulting in different reaction products. In DMF and DMSO only diamagnetic yellow species is formed, showing intense absorbance at 335 nm, while in An formation of blue paramagnetic product is observed, absorbing at 520 and 740 nm. It should be mentioned, however, that the paramagnetic species formed in these conditions could not be stabilized. In contrast to water solutions where kinetically stable paramagnetic complexes are obtained, the concentration of the blue paramagnetic species formed in An slowly decreased and after a week was very low.

In water-methanol medium (1:2 v/v) a red diamagnetic platinum complex was obtained, absorbing at 390 and 580 nm.

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