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Green–Blue Platinum–Urea Complexes*

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Abstract

The reaction of urea with K_2PtCl_4 and the formation of a non-stoichiometric olive green complex is reported. The complex has been studied by infrared, Raman, UV and ^{195}Pt NMR spectroscopy and by chemical methods.

Introduction

The platinum blue complexes were discovered in 1908 by Hofman and Bugge [1]. However, Kournakov [2] briefly described these compounds as early as 1895. The platinum blues later proved to be not well defined products [3, 4]. The renewed interest in platinum blues has arisen from the recent discovery [5] of the blue–green compounds obtained upon reaction of the hydrolyzed drug, *cis*-dichlorodiammineplatinum (cis-DDP) with pyrimidine bases to form platinum–pyrimidine blue complexes.

It is known that urea acts with the platinum salt K_2PtCl_4 in a 2:1 ratio to form stable and well defined yellow complexes of the formula $PtCl_2(urea)_2$ [6]. The present work describes a new platinum–urea, blue–green complex of not well defined stoichiometry. We have studied the UV–Vis, IR, Raman and ^{195}Pt NMR spectra of this newly synthesized Pt–urea complex. The complex has shown antibiotic and antibacterial activity and should be studied further for other biomedical applications. Platinum toxicity seems to be reduced in the presence of urea, just as antimony toxicity is reduced with the formation of an antimony salt of urea [7]. A urea–stibamine salt has been used successfully in the antimony treatment of a kala-azar epidemic in the past [7].

Experimental

Preparation of the Platinum–Urea Complex

The complex was prepared by reacting urea with K_2PtCl_4 in ethanol. The method was a modification of the method of Dechael [8] used to prepare the yellow dichlorobis(urea)platinum(II). A water solution of potassium tetrachloroplatinate(II) (0.15 M) was added to 0.3 M urea in water and heated at 100 °C for 10 min. The color of the solution changed from blood red (K_2PtCl_4) to a deep chocolate brown. The original pH of the solution was 6 and dropped to 2. The color changed further with time to dark olive green and the pH returned to 6. The solution was cooled to 25 °C and 20 vol. of 100% ethanol were added. It was then centrifuged and the precipitate was washed twice with 90% ethanol and dried under vacuum at 25 °C yielding a dark greenish-blue powder. The powder (1 g) was dissolved in water (5 ml), 10 vol. of ethanol (100%) were added then centrifuged, and dried under vacuum at room temperature. The yield of 0.2 g represents about 30% of the weight of K_2PtCl_4. The complex is highly soluble in water and in physiological saline, giving a blue-greenish color. On evaporation from a water solution it shows needle-like crystals, but they were very small for X-ray diffraction analysis. The absorption spectrum of the solution shows a maximum at $\lambda_{max} = 725$ nm with a shoulder at 600 nm and it obeys Beer's law unlike the platinum blues reported in the literature [5]. The complex is stable in neutral or alkaline solutions. Melting point experiments show change of color above 290 °C. Conductivity measurements in water indicate three ions in solution, $\Lambda_\infty = 310\ M^{-1}\ ohm^{-1}\ cm^2$ for a molar conductivity measured at a concentration of 0.001 M. A water solution on prolonged exposure to light slowly forms insoluble platinum black. Analytical results are not conclusive as to the stoichiometry of the compound.

Fourier Transform Infrared (FT-IR) and Raman Spectra

FT-IR spectra were obtained with a Nicolet 7199 FT-IR and a Digilab Model FTS-15C with a large

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*This article is dedicated to our colleague P. K. Ganguli who passed away.

†Deceased.

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scope dual speed. The Fourier Transform Infrared Spectrometer was equipped with a computer and a data system and employed potassium bromide and polyethylene windows. The spectra of the solid complex were obtained by means of the potassium bromide disk technique and by measurements in Nujol mulls between polyethylene plates. The Raman and resonance Raman spectra of solid compound and water solutions of it were obtained with a SPEX 1400 spectrophotometer equipped with Ar$^+$ laser. Intensity measurements of the Raman bands were obtained with respect to NaClO$_4$ as internal standard.

Results

The FT-IR and Raman results of the Pt–urea complex are given in Tables 1 and 2. The far infrared spectrum (50–500 cm^{-1}) of the complex is shown in Fig. 1. The Raman and pre-resonance Raman spectra (1700–200 cm^{-1}) are shown in Figs. 2 and 3. The pre-resonance Raman data are given in Table 3. As is shown in Table 1 several bands of urea are shifted considerably upon complexation with platinum in the 1700–1600 cm^{-1} region. The carbonyl amide frequency (amide I) of the Pt–urea complex is observed at 1680 cm^{-1} in the infrared spectrum which on partial deuteration moves to 1660 cm^{-1}. The band at 1610 cm^{-1} loses intensity and shifts slightly on deuteration. There are important shifts also in the region 1500–800 cm^{-1}. The free urea band at 1465 cm^{-1} shifts to 1385 cm^{-1} in the spectra of the Pt–urea complex, which also shifts slightly on deuteration. A new band is observed at 1280 cm^{-1} in the complex. On the other hand the band at 1150 cm^{-1}

TABLE 1. FT-IR Bands of Urea and Pt–Urea Complex

Urea	Pt–Urea	Assignment
	3560s	ν(O–H) water of cryst.
3450vs	3450vs	ν(NH$_2$) antisym. free
3345s	3340s	ν(NH$_2$) sym. free
3250s	3220s	ν(NH$_2$...H-bonded)
1680s	1680vs	ν(C=O) + δ(NH$_2$) antisym. (amide I)
1610vs	1610s	ν(C=O) + δ(NH$_2$) sym.
1600ms	1585ms	δ(NH$_2$) (amide II)
1470s	1385	ν(C=N) antisym. (amide III)
	1280	
1150s	1180s	r(NH$_2$)
	1130sh	
1060m	1044w	ν(C–N)
1005m	1000w	
	918m	
790m	810m	δ(–NH–) out-of-plane def.
720m	690m	δ(C=O) out-of-plane def.
560s	565ms	δ(NCO)
	525m	ν(Pt–N) antisym.
490ms	500ms	δ(NCN)
	404m	ν(Pt–N) antisym.
370vs		w(NH$_2$)
	325vs	ν(Pt–Cl)
	195s	δ(ClPtCl)δ(ClPtN) def.
175vs	175s	δ(CN)
100s	115s	lattice
68s	90s	vibrations

s = strong, vs = very strong, m = medium, ms = medium strong, sh = shoulder, ν = stretch, δ = def., r = rocking, w = wagging.

TABLE 2. Raman Frequencies in cm^{-1} of Urea and Pt–Urea Complex

Urea	Pt–Urea	Assignment
1655m	1655m	ν(C=O) + δ(NH$_2$) antisym. (amide I)
1590w	1590w,br	ν(C=O) + δ(NH$_2$) sym.
1545m		δ(NH$_2$) (amide II)
1480w	1480w	ν(C=N) antisym. (amide III)
	1210sh	
1180m	1180m	
	1150sh	r(NH$_2$)
1020vs	1060m	ν(C–N)
	800m	δ(NH) out-of-plane
550s	600s	δ(NCO)
490m	490vs	δ(NCN)
	440vs	ν(Pt–N) sym.
380w		
	330sh	ν(Pt–Cl)

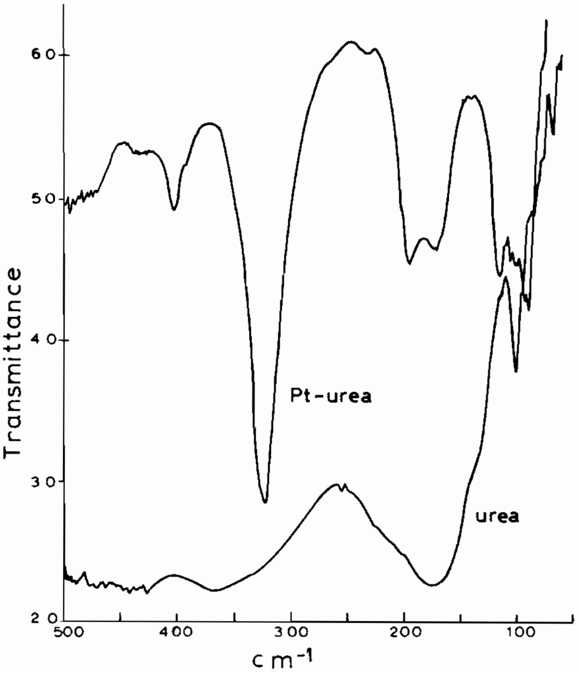


Fig. 1. Far infrared spectra of urea and Pt–urea complex, 500–50 cm^{-1}.

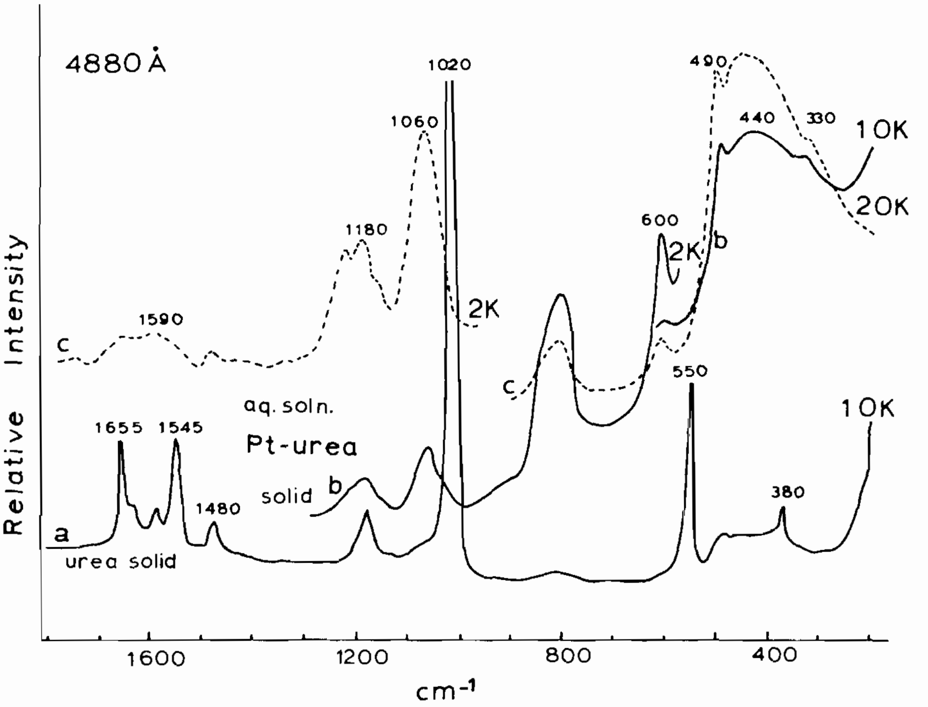


Fig. 2. Raman spectra of urea and Pt–urea complex: (a) urea solid, taken with 10 K energy; (b) Pt–urea complex solid; (c) Pt–urea complex solution, broken lines, taken at various energies 2, 10 and 20 K. Excitation wavelength 4880 Å.

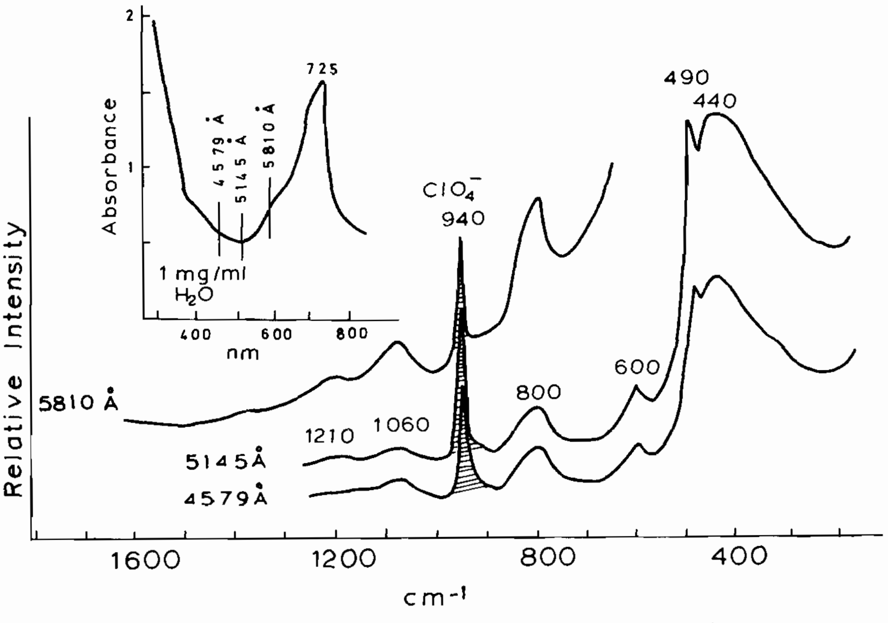


Fig. 3. Pre-resonance Raman spectra of the Pt–urea complex at three wavelengths, λ = 5810, 5145 and 4579 Å. The insert shows the electronic spectrum of Pt–urea and the relation of the absorption band at 724 nm to the excitation wavelength λ.

of free urea shifts to higher frequencies near 1180 cm^{-1}. In the IR spectrum of the complex there is also a band near 1000 cm^{-1} and a medium intensity band near 918 cm^{-1}, as well as the medium bands at 810 and 600 cm^{-1}. The band at 525 cm^{-1} in the Pt–urea complex is new as well as the bands at 400 (Raman) and 404 (IR). New Pt–urea bands below 380 cm^{-1} are observed at 325 and 195 cm^{-1}, in addition to the lattice vibrations below 150 cm^{-1}.

TABLE 3. Resonance Raman Bands as a Function of Excitation Wavelength Frequencies (ν) in the Platinum–Urea Complex Together with the Intensity Ratios ($I\nu/I_{940}$)[a]

λ (Å)	ν				
	440	490	600	800	1060
4579	1.163	1.163	0.174	0.290	0.140
5145	1.417	1.426	0.217	0.200	0.070
5810				0.823	0.367

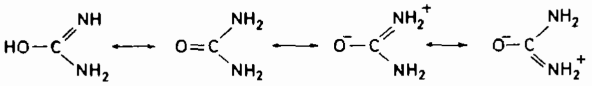
[a] $I\nu$, Intensity of frequency ν; I_{940}, intensity of the internal standard ClO_4^- band at 940 cm^{-1}.

In the Raman spectrum of the Pt–urea complex the carbonyl–amide band is observed unchanged at 1655 and 1590 cm^{-1}, whereas the band of free urea at 1545 cm^{-1} disappears in the Raman spectrum of the Pt–urea complex. The Raman spectrum of the Pt–urea complex shows a new band near 1210 cm^{-1}, as a shoulder, and another at 800 cm^{-1}. Free urea shows Raman bands at 550, 490 and 370 cm^{-1}. The first two bands are observed in the Pt–urea complex spectrum at 600 and 490 cm^{-1}, whereas the band at 370 cm^{-1} is masked by the strong and large Raman band near 440 cm^{-1}. Also a new band is observed at 330 cm^{-1}. Tentative assignments of these bands are given in Tables 1 and 2.

In Table 3 and Fig. 3 are given the pre-resonance Raman spectra as a function of excitation wavelength. The intensities of the bands were calculated from the peak heights and compared to an internal standard (ClO_4^-). In the insert of Fig. 3 is shown the electronic spectra and the lines of excitation for the Pt–urea complex. The ratios of the three bands at 440, 490 and 600 cm^{-1} are increasing by approaching the absorption band at 725 nm, whereas those of 800 and 1060 cm^{-1} go through a minimum and then increase. The intensity ($I\nu$) of excitation with 5810 Å could not be measured for the first three bands, being too large.

Discussion

The structure of urea is believed to be resonating between the following limiting forms [9–13]



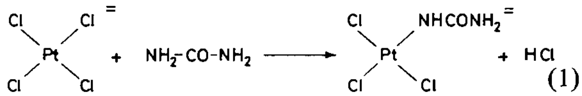
I enol — **II** keto — **III** — **IV** zwitterionic structures

The majority of metals in the periodic table form complexes with urea through coordination of the carbonyl oxygen atom [13]. This coordination should favour forms **I**, **III** and **IV** with a decrease of the C=O bond order and an increase of the C=N bond order. This has not been observed here. On the other hand, coordination through the nitrogen atom of urea would favour structure **II** (free base) with an increase of ν(C=O) and a decrease of ν(C–N). Furthermore, coordination by a metal through –NH of structure **I** should involve considerable changes in the vibrations of urea as is shown here (see Spectra and Tables). Assignment of urea vibrational frequencies has been reported [9, 10, 13–16]. The presence of a carbonyl amide vibration at 1680 cm^{-1} (amide I) in the infrared spectrum of the Pt–urea complex here suggests that coordination of the platinum atom is not through the carbonyl oxygen. The coordination could be through the amide or imine group; this fact is also supported by the reduction of the 1610 cm^{-1} band intensity together with the decrease of the ν(C–N) frequency from 1465 to 1385 cm^{-1} in the complex. The new band at 1280 cm^{-1} may be assigned to a (–NH–) bound to the metal by liberation of H^+. The 1150 cm^{-1} band which is assigned to an NH_2 rocking increases to 1180 cm^{-1} (IR) upon complexation of this group with a shoulder at 1150 cm^{-1} (Raman). The ν(C–N) vibration is modified upon linkage to platinum (Tables 1 and 2) and on complexation the strong Raman band of free urea at 1020 cm^{-1} increases to 1060 cm^{-1}, which implies that platinum may be bound to nitrogen.

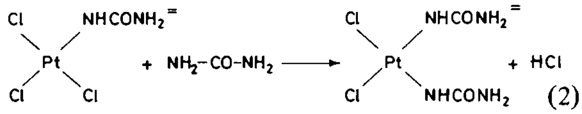
The medium intensity infrared bands of free urea at 790 and 720 cm^{-1} have their corresponding bands in the Pt–urea complex at 810 and 690 cm^{-1}, whereas in the Raman spectrum only one band is observed for the Pt–urea complex at 800 cm^{-1}. These two bands may be assigned to NH_2 and C=O out-of-plane bending [13]. The infrared band at 560 cm^{-1} and the Raman at 550 cm^{-1} of free urea assigned to δ(NCO) have their corresponding bands in the spectrum of the complex at 565 (IR) and near 600 (Raman) cm^{-1}. The infrared band of urea at 490 cm^{-1} assigned to δ(NCN) is shown at 500 cm^{-1} in the Pt–urea complex, whereas in the Raman spectrum this band does not change. The new infrared band at 525 cm^{-1} in the Pt–urea spectrum is assigned to a ν(Pt–N) assymmetric stretch, whereas the symmetric ν(Pt–N) stretch is observed in the Raman spectrum at 440 cm^{-1}. The low frequency bands in the spectrum of Pt–urea at 325 (IR) and 330 (Raman) cm^{-1} are new bands for the complex and are assigned to the ν(Pt–Cl) stretch (see Tables 1 and 2). Moreover, the new band at 195 cm^{-1} could be assigned to a vibration involving the platinum and chlorine atoms, i.e. δ(ClPtN) deformation and that the 175 cm^{-1} band in both free and bound urea is assigned to a skeletal deformation of the ligand urea, δ(CN).

Possible Structure of the Platinum–Urea Complex

Both infrared and Raman spectra are consistent with a platinum bound to the nitrogen of urea and that the bound nitrogen seems to be an imino group (–NH–), i.e $K_2[PtCl_2(NHCONH_2)_2]$ (monomer). A proton liberation is observed during the preparation of the olive green color complex together with a decrease of the pH from 6 to 2. The reaction may proceed as follows

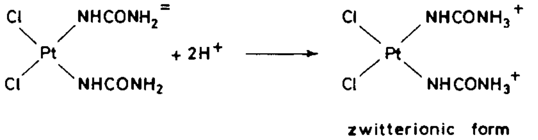


(1)



(2)

Upon standing in water solution the pH returns to 2, which may be due to protonation of NH_2 and formation of the following zwitterionic salt



The synthesized Pt–urea complex is extremely soluble in water, which is expected for an ionic complex, $K_2[PtCl_2(NHCONH_2)_2]$. Conductivity measurements in water indicate three ionic species in solution and ^{195}Pt NMR measurements are indicative of a platinum species with two chlorides and two nitrogen atoms around the platinum atom [16, 17]. The ^{195}Pt NMR shows one sharp peak at $\delta = -1653.8$ ppm (300 K) as compared to K_2PtCl_4 taken as a reference [17]. Increase of temperature by 10 K shifted the NMR peak to $\delta = -1641.17$ ppm which is consistent with the above formula. The changes in the IR and Raman spectra suggest the formation of a $Pt–NH–CONH_2$ bond with deprotonation of the amide group. The changes in the 1600, 1280, 1180 and 790 cm^{-1} bands are similar to the amide complexes studied by Gillard and Wilkinson [3] and suggest the presence of an –NH– group together with a carbonyl group. However, the formation of polymeric species keeping the carbonyl group uncoordinated is possible considering the UV spectra, which are indicative of an oligomeric complex.

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