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높은 온도에서 Urea와 금속이온과의 반응으로 얻어진 금속 Complexes의 합성과 분광학적 연구

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Synthesis and Spectroscopic Studies of Metal Complexes Formed in the Reaction of Metal Ions with Urea at High Temperature

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요 약. Urea는 높은 온도(60~80 °C)의 수용액 상태에서 $PtCl_2$, $H_2[PtCl_6]\cdot 6H_2O$, $H_2[IrCl_6]$ $Ni(CH_3CO_2)_2$ 와반응해서 각각 (**1**)$[PtCl_2(Urea)]\cdot 2H_2O$, (**2**)$(NH_4)_2[PtCl_6]$, (**3**)$(NH_4)_2[IrCl_6]\cdot H_2O$, (**4**)$[Ni_2(OH)_2(NCO)_2(H_2O)_2]$의 complexes를 생성한다. complexe **1**에서 urea는 중성 bidentate 리간드로써 Pt(II)와 배위한다. complexe **2**,**3**,**4**에서는 높은 온도에서 반응하는 동안 배위 urea분자들이 분해되고 다양한 반응생성물들을 얻을 수 있다. 모든 complexes은 각각 적당한 수득률로 dark green(**1**) yellow(**2**), pale brown (**3**) faint green(**4**)의 침전물로 분리된다. 반응생성물은 열분석, IR, ^1H and ^{13}C NMR spectra에 의해 측정 되었다. 이 complexes의 구성을 설명하는 일반적인 메카니즘이 제시되었다.

주제어: 합성, Urea, Platinum, Nickel, Iridium, IR, NMR Spectra, 열분석

ABSTRACT. Urea reacts with $PtCl_2$, $H_2[PtCl_6]\cdot 6H_2O$, $H_2[IrCl_6]$ and $Ni(CH_3CO_2)_2$ in aqueous solution at high temperature (60-80 °C) yielding $[PtCl_2(Urea)]\cdot 2H_2O$ (**1**), $(NH_4)_2[PtCl_6]$ (**2**), $(NH_4)_2[IrCl_6]\cdot H_2O$ (**3**) and $[Ni_2(OH)_2(NCO)_2(H_2O)_2]$ (**4**) complexes, respectively. In complex **1**, urea coordinates to Pt(II) as a neutral bidentate ligand *via* amido nitrogen atoms. In complexes **2**, **3** and **4** it seems that the coordinated urea molecules decompose during the reaction at high temperature and a variety of reaction products are obtained. All complexes were isolated in moderate yields as dark green (**1**), yellow (**2**), pale brown (**3**) and faint green (**4**) precipitates, respectively. The reaction products were characterized by their micro-analysis, IR, ^1H and ^{13}C NMR spectra as well as thermal analysis. General mechanisms describing the formation of these complexes were suggested.

Keywords: Synthesis, Urea, Platinum, Nickel, Iridium, IR, NMR Spectra, Thermal Analysis

INTRODUCTION

From a coordination chemistry prospective, urea could potentially be a neutral ligand for transition metals and coordinates as a monodentate either via its oxygen[1] or nitrogen atoms[2] or as a bidentate chelating or bridging ligand depending on the type of metal ion.[2-5] Biologically, many hydrolytic enzymes employ two metal ions to facilitate the concentrated binding of substrate and addition or elimina-

tion of water.[6-8] Urease is a nickel-dependent mtalloenzyme that catalyzes the hydrolysis of urea to ammonia and carbon dioxide.[4] Urease employs a nonequivalent pair of nickel ions to facilitate the concerted binding of the substrate at one center and nucleophilic attack of water or hydroxide at the other center.[9-11]

The reactions between various transition metal ions with urea at room temperature have been studied extensively and many metal–urea complexes have been isolated and characterized.[12-16] Recently, we have found that reaction of urea with various metal ions at high temperature proceeds with different mode in which the coordinated urea molecules decompose and a variety of reaction products have been obtained.[17-23] The rule played by metal ions in decomposing coordinated urea seems to be depending upon the type of metal ion and the nature of the counter ions involved in the reaction as well as on the reaction temperature.

The present investigation was reported to study the course of the reaction of urea with $PtCl_2$, $H_2[PtCl_6]\cdot 6H_2O$, $H_2[IrCl_6]$ and $Ni(CH_3CO_2)_2\cdot 4H_2O$ at *ca.* 60-80 °C. The reaction products were characterized by their elemental analyses, infrared, ^1H and ^{13}C NMR spectra as well as thermal analysis. The obtained complexes are identified as $[PtCl_2(Urea)]\cdot 2H_2O$ (**1**), $(NH_4)_2[PtCl_6]$ (**2**), $(NH_4)_2[IrCl_6]\cdot H_2O$ (**3**) and $[Ni_2(OH)_2(NCO)_2(H_2O)_5]$ (**4**), respectively.

EXPERIMENTAL

All of the chemical used throughout this investigation were extra pure grade and used without further purification.

Infrared spectra of the reactants and the obtained complexes were recorded from KBr discs (4000-400) using a Buck scientific 500-IR spectrophotometer. Thermal gravimetric analysis (TG) and (DTG) were carried out using a Perkin-Elmer TGA-7 computerized thermal analysis system. The rate of heating of samples was kept at 10 °C min^{-1}. Sample mass of 0.397 mg was analysed under N_2 flow of 30 ml min^{-1}. Microanalyses were performed by the Microanalysis Unit of Cairo University, Egypt using CHNS-932 (LECO) and vario-EL (elmentar Analysensysteme) elemental analyzers.

^1H and ^{13}C NMR spectra were recorded on Varian spectrometers Gemini 200, VXR 400 and Unity 500 operating at 200, 400 and 500 MHz for ^1H, respectively. Solvent signals (^1H, ^{13}C) were used as internal references.

$[PtCl_2(Urea)]\cdot 2H_2O$ (1)

To a suspension of platinum(II) chloride (0.531 g, 0.01 mol) in 10 ml of distilled water, a solution (10 ml) of urea (0.720 g, 0.06 mol) was added. The mixture was stirred at room temperature for about 24 h. The obtained clear solution was then stirred for about 8 h at *ca.* 60 °C (in a water bath). The resulting precipitate of $[PtCl_2(Urea)]\cdot 2H_2O$ (**1**) (dark green) was then filtered out, washed several times with hot distilled water and dried at 50 °C in an oven for 3 h and then in a desiccator in *vacuo*. Yield: 0.465 g (64.3%).

Anal. found: C, 3.29; H, 2.35; Cl, 18.98; N, 7.84.

Anal. calc. for $CH_8Cl_2N_2O_3Pt$ (362.07): C, 3.32; H, 2.23; Cl, 19.58; N, 7.74.

$(NH_4)_2[PtCl_6]$ (2)

To a solution, (5 ml) of $H_2[PtCl_6]\cdot 6H_2O$ (0.518 g, 0.01 mol) in water, a solution (10 ml) of urea (0.360 g, 0.06 mol) was added. The resulting clear yellow solution was stirred for about 8 h at *ca.* 60 °C (in a water bath). The resulting yellow precipitate of compound **2** was filtered off, washed several times with hot distilled water and MeOH and then dried in a desiccator in *vacuo*. Yield: 0.190 g (42.8%).

Anal. found: Cl, 45.94; H, 1.96; N, 6.05.

Anal. calc. for $Cl_6H_8N_2Pt$ (443.87): Cl, 47.92; H, 1.82; N, 6.31.

$(NH_4)_2[IrCl_6]\cdot H_2O$ (3)

To a water solution (10 ml) of $H_2[IrCl_6]$ (0.814 g, 0.01 mol), a solution (10 ml) of urea (0.720 g, 0.06 mol) was added. The resulting clear solution was stirred for about 8 h at *ca.* 65 °C (in a water bath), there was changing in colour of the reaction mixture from dark brown to red. The precipitate of compound (**3**) (pale brown) was then obtained by

the addition of acetone dropwisly with stirring that was filtered off, washed several times with acetone and then dried in a desiccator in *vacuo*. Yield: 0.103 g (11.2%).

Anal. found: Cl, 45.58; H, 2.50; N, 6.55.

Anal. calc. for $Cl_6H_{10}IrN_2O$ (459.03): Cl, 46.34; H, 2.20; N, 6.10.

$[Ni_2(OH)_2(NCO)_2(H_2O)_2]$ (4)

To a solution (20 ml) of nickel(II) acetate tetrahydrate, $Ni(CH_3CO_2)_2{\cdot}4H_2O$ (0.498 g, 0.01 mol) in water, a solution (20 ml) of urea (0.720 g, 0.06 mol) was added. The clear solution was stirred for about 4-6 h at *ca.* 80 °C (in a water bath) resulting in precipitation of a faint green compound that was filtered off, washed several times with hot distilled water, dried at 50 °C in an oven for 4 h and then in a desiccator in *vacuo*. Yield: 0.200 g (36.8%).

Anal. found: C, 9.01; H, 2.41; N, 9.84.

Anal. calc. for $C_2H_6N_2Ni_2O_6$ (271.47): C, 8.85; H, 2.23; N, 10.32.

RESULTS AND DISCUSSION

Urea reacts with platinum(II) chloride in aqueous solution at 60 °C to form a dark green complex identified as $[PtCl_2(Urea)]{\cdot}2H_2O$ (**1**). In this complex, urea coordinates to Pt(II) as a bidentate chelating ligand *via* its nitrogen atoms. The infrared spectrum of the complex shows the characteristic bands of N-coordinated urea. Assignments of the infrared bands in the complex spectra in comparison with those of free urea were given in *Table* 1. The formation of N→Pt coordination bond causes significant changes in many of characteristic urea vibrations. The N-H stretching vibrations are shifted to lower values[24]. On the other hand, the observed stretching vibration of the carbonyl group, n(C=O) in the complex spectrum is shifted to a higher value indicating that oxygen atom is not the donor site, see *Table* 1. Furthermore the stretching vibration, ν(N-C) was observed at a lower frequency (1390 cm^{-1}) in comparison with its corresponding value in free urea (1463 cm^{-1}). This is in consistent with the previously known[3] for N-coordinated urea. The

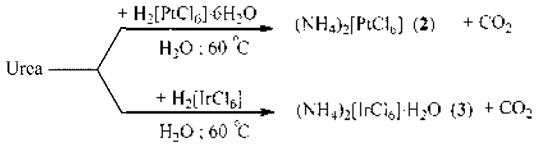
Table 1. Characteristic infrared frequencies (cm^{-1}) and tentative assignments for urea and complex 1, $[PtCl_2(Urea)]{\cdot}2H_2O$

Urea	$[PtCl_2(Urea)]{\cdot}2H_2O$	Assignments**
	3410 vs	ν(O–H); H_2O
3458 vs		
3346 vs	3292 vs	
3256 m	3174 vs	ν(N–H); NH_2
1677 vs	1716 s	ν(C=O)
1620 vs	1615 vs	δ_s(N–H); NH_2
	1588 vs	$\delta_s(H_2O)$
1463 vs	1390 s	ν_{as}(C–N)
1360 vw		
1150 s	1184 m	$\delta_r(NH_2)$
1068 sh	-	ν_s(C–N)
999 w	-	$\delta_w(NH_2)$
833 vw		
787 w	-	out-of-plane δ (C=O) def
553 vs		
492 vs	535 m	δ(NCN)
	315 m	ν(Pt–N)

*s, strong; m, medium; v, very; w, weak; sh, shoulder.
**ν, stretching; as, asymmetric; s, symmetric; δ_b, bending; δ_r, rocking; δ_w, wagging.

deformation (bending and in-pane rocking) motions of NH_2 group are observed at 1615 and 1184 cm^{-1}, respectively. The appearance of only one band in the region characteristic for the bending vibration of NH_2 at 1615 cm^{-1} indicate that both NH_2 groups are coordinated to Pt(II) ion and urea acts as chelating ligand.[25] The geometry associated with complex is likely square planar with two chloro and two nitrogens constituting the coordination sphere of platinum(II) ion. This conclusion was also supported by the data obtained from ^1H and ^{13}C NMR measurements. *Table* 4. Only one signal is observed in ^1H NMR spectrum of $[PtCl_2(Urea)]{\cdot}2H_2O$ complex and strongly down field shifted (7.36 ppm) in comparison with its value in free urea (5.64 ppm). Further more the ^{13}C NMR spectra of the complex and free urea show only one signal at approximately the same value. These two observations are consistent with a chelating bidentate nature for urea through the two nitrogen atoms.

Urea seems to interact with hexachloroplatinic or hexachloroiridic acid in a different mode giving



Scheme 1.

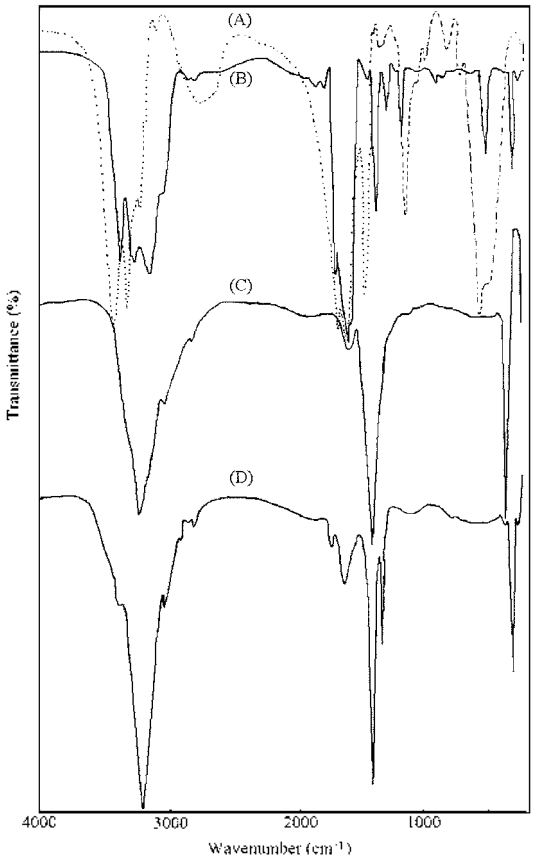


Fig. 1. IR spectra of (A) urea, (B) Complex 1, (C) Complex 2 and (D) Complex 3.

complexes **2** and **3**, respectively. The formation of such complexes upon heating of an aqueous mixture of urea with $H_2[PtCl_6]$ and $H_2[IrCl_6]$, (see *Scheme* 1), were clearly identified from their infrared and ^1H NMR spectra (*Fig.* 1, *Tables* 2, 4). The asymmetric and symmetric stretching motions for N-H were observed at lower frequencies in both complexes, *Table* 2, in comparison with their values in free urea and in consistent with those known for ammonium ion.[3,6-29] Such way of interaction was further supported by observing the stretching motion for M-Cl bond in $[PtCl_6]^{2-}$ and $[IrCl_6]^{2-}$ moieties at 337 and 306 cm^{-1}, respectively [30]. ^1H NMR spectra of the complexes $(NH_4)_2[PtCl_6]$ and $(NH_4)_2[IrCl_6]\cdot H_2O$ strongly support this conclusion, there is no signals correspond to urea observed but instead a new broad singlet signal around 7.3 ppm assigned to NH_4^+ is observed.

Table 2. Characteristic infrared frequencies (cm^{-1}) and tentative assignments for complexes $(NH_4)_2[PtCl_6]$ (**2**) and $(NH_4)_2[IrCl_6]\cdot H_2O$ (**3**)

$(NH_4)_2[PtCl_6]$	$(NH_4)_2[IrCl_6]\cdot H_2O$	Assignments**
-	3403 sh	υ(O–H); H_2O
3238 vs, br	3209 vs	υ_{as}(N–H); NH_4^+
3042 m	3040 m	υ_s(N–H); NH_4^+
1590 m	1623 m	$\delta_{as}(NH_2)$; NH_4^+
1401 vs	1403 vs	$\delta_s(NH_2)$; NH_4^+
-	1322 s	$\delta_s(H_2O)$
337 vs	306	υ(M–Cl)

*s, strong; m, medium; v, very; w, weak; sh, shoulder.
**υ, stretching; as, asymmetric; s, symmetric; δ_{as}, bending; δ_s, twisting.

The catalytic decomposition of urea in presence of hexchloroplatinic or hexachloroiridic acids could be explained as follows:

$$NH_2CONH_2 + H_2O \rightarrow NH_2CO_2^- + NH_4^+$$
$$NH_2CO_2^- + 2H^+ \rightarrow NH_4^+ + CO_2$$

An aqueous solution of nickel(II) acetate was found to interact with urea at *ca.* 80 °C and a faint green powder precipitate of complex (4) is obtained. The complex was isolated in a good yield and identified by microanalysis, IR, ^{13}C NMR spectra and thermal analysis. The IR spectrum of the complex **4** is shown in *Fig.* 2A and its band assignments are given in *Table* 3. The infrared spectrum shows no bands either due to coordinated urea or acetate ions but instead a group of bands characteristic for coordinated isocyanato, coordinated water molecules and bridged hydroxo groups. The complex spectrum show the presence of bands characteristic for coordinated terminal isocyanato group at 2240 and 2080 cm^{-1} at higher wavenumbers as expected in comparison with the corresponding bridged isocyanato ions.[3,20,35] The stretching vibration of the

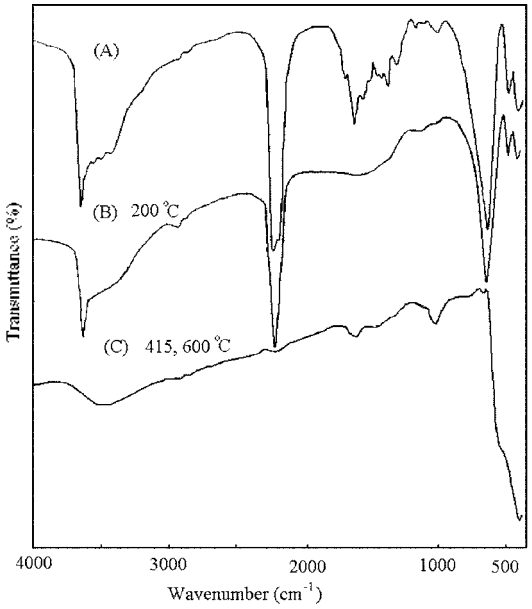


Fig. 2. IR spectra of : (A) complex **4** (B) The residue left after the first stage (200 °C), $[Ni_2(OH)_2(NCO)_2]$, (C) The final thermal decomposition product, NiO.

Table 3. Characteristic infrared frequencies (cm^{-1}) and tentative assignments for complex **4**. $[Ni_2(OH)_2(NCO)_2(H_2O)_2]$

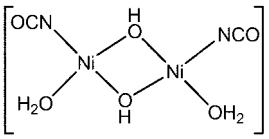
$[Ni_2(OH)_2(NCO)_2(H_2O)_2]$	Assignments**
3633 s	ν(O–H)
3444 m	ν_{as}(O–H); H_2O
3381 w	ν_s(O–H); H_2O
2240 vs	ν_{as}(NCO^-)
2080 sh	ν_s(NCO^-)
1693 sh	δ_s(H_2O)
1618 m	δ_{as}(H_2O)
1306 w	δ_t(H_2O)
1155 w	δ_b(M–O–H)
1017 w	δ_r(H_2O)
634 vs	δ(NCO^-)
478 m	ν(Ni–O)
393 m	ν(Ni–N)

*s, strong; m, medium; v, very; w, weak; sh, shoulder.
**ν, stretching; as, asymmetric; s, symmetric; δ_b, bending; δ_r, twisting, δ_r, rocking.

hydroxo group was observed as a strong band at 3633 cm^{-1} and for coordinated water in the 3444-3381 cm^{-1} region.[36-38] Tentative assignments of bands associated with bending motions of NCO^-, OH^- and H_2O ligands were listed in *Table* 3. Another group of bands lying at lower wavenumbers 478-393 cm^{-1} associated with the vibrational motions of Ni-O and Ni-N bonds were also observed [39]. ^1H and ^{13}C NMR spectra of the complex $[Ni_2(OH)_2(NCO)_2(H_2O)_2]$ shows no signals due to free or coordinated urea, but instead a new signal at 124.0 in the ^{13}C NMR spectrum is observed corresponds to NCO ligand. Based on this data together with the elemental and thermal analysis we identified the obtained product as binuclear nickel(II) complex, $[Ni_2(OH)_2(NCO)_2(H_2O)_2]$ and the most probable structure associated with this formula is shown in Formula 1.

Table 4. Selected ^1H and ^{13}C NMR chemical shifts (δ in ppm) of urea and its compounds in dmso-d_6

Compound	δ (^1H)	δ (^{13}C)
Urea	5.64 (s, br, NH_2)	160.7 (s, CO)
$[PtCl_2(Urea)]\cdot 2H_2O$	7.36 (br, Pt–NH_2)	158.2 (s, CO)
$[Ni_2(OH)_2(NCO)_2(H_2O)_2]$	-	124.0 (s, NCO)
$(NH_4)_2[PtCl_4]$	7.31 (br, NH_4^+)	-
$(NH_4)_2[IrCl_6]\cdot H_2O$	7.30 (br, NH_4^+)	-



Formula 1

It is well known that urea coordinates to Ni(II) ions at room temperature forming the $[Ni(urea)_4]^{2-}$ complex ion.[2,30-32] At high temperature the following reaction may take place:

$$2[Ni(Urea)_4](CH_3CO_2)_2 + 10\,H_2O \xrightarrow{80^{\circ}C} [Ni_2(OH)_2(NCO)_2(H_2O)_2]\ (\mathbf{4}) + 4CH_3CO_2H + 6CO_2 + 14NH_3$$

The catalytic decomposition of urea and the formation of NCO^- group in presence of nickel acetate salt could be explained as follows:[33,34]

$$NH_2CONH_2 + H_2O \rightarrow NCO^- + NH_4^+$$
$$NH_4^+ + H_2O \rightarrow NH_3 + H^-$$

Thermogravimetric (TG) and derivative of thermogravimetric analysis (DTG) were carried out for complex **4** under N_2 flow, *Fig.* 3. The obtained ther-

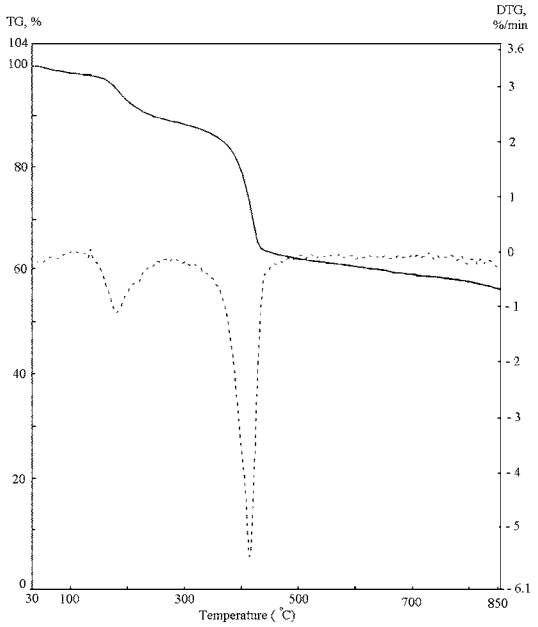


Fig. 3. Thermogravimeteric (TG) and derivative (DTG) of complex **4**.

mal data strongly support the proposed complex formula and indicate that the mode of thermal decomposition occurs in two stages. The first stage lies at a maximum temperature of 175.6 °C and is accompanied by a weight loss of 13.4% corresponding to the loss of two water molecules in consistent with the calculated value of 13.26%. The infra red spectrum obtained for the residue at this stage (at 200 °C) clearly show the disappearance of bands due to water molecules and the presence of the characteristic bands due to OH- and NCO-groups, see *Fig.* 2B. The second stage was observed at 414.0 °C and is accompanied by a weight loss of 31% associated with the loss of two HNCO units in good agreement with the calculated values of 31.17% according to the following reactions:

$$[Ni_2(OH)_2(NCO)_2(H_2O)_2] \xrightarrow{175.6^{\circ}C} [Ni_2(OH)_2(NCO)_2] + 2H_2O$$

$$[Ni_2(OH)_2(NCO)_2] \xrightarrow{414.0^{\circ}C} 2NiO + 2HNCO$$

The infrared spectrum for the final residue left after this temperature strongly supports this conclusion see *Fig.* 2C. The spectrum shows only the characteristic bands associated with NiO.

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