Inorganica Chimica Acta, *164* (1989) 201–204

Structure of Ni(II)–Creatinine Complex Species Formed in Non-aqueous Media

M. MITEWA, G. GENCHEVA, P. R. BONTCHEV*
Department of Chemistry, University of Sofia, 1126 Sofia (Bulgaria)
E. ZHECHEVA
Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia (Bulgaria)
and V. NEFEDOV
Institute of General and Inorganic Chemistry, U.S.S.R. Academy of Sciences, 117071 Moscow (U.S.S.R.)

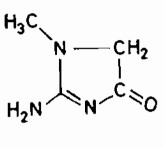
(Received February 27, 1989; revised May 29, 1989)

Abstract

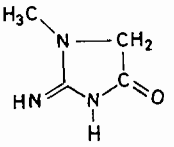
Three different types of Ni(II)–creatinine complexes are synthesized in organic media. It was proved that the complexes are formed only in non-aqueous media and their dissolution in water is connected with immediate dissociation. The three complexes were studied using spectroscopic (IR, EPR, ESCA) magnetochemical and thermogravimetric methods. An octahedral structure and different contents of creatinine molecules in their inner coordination spheres were assumed.

Introduction

Our systematic studies on the complexation ability of the bioligand creatinine (**I** and **II**) towards Cu(II), Pt(II), Pt(III) and Pd(II) [1–5] have shown the strong influence reaction conditions have on complexation [2–5]. On the other hand our preliminary investigations proved a rather surprising fact – no complex formation proceeded between Ni(II) and creatinine in water medium, Taking into account, however, the excellent coordination properties of creatinine [1–7] it was assumed that Ni(II)–creatinine complex formation might be realized through a change of the reaction medium. In the present paper the data obtained for the formation of three different Ni(II) complexes and their structures are reported. Complex formation was studied in organic solvents with different polarity: methanol, acetone, acetonitrile (An), methylacetamide (MAA).



I



II

Experimental

Synthetic and Analytical Procedures

$[Ni(creat)_4(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (1) (creat = creatinine) (green)

A total of 0.5 mmol (0.1454 g) $Ni(NO_3)_2 \cdot 6H_2O$ and 3.0 mmol (0.3393 g) creatinine (molar ratio 1:6) was dissolved in 20 cc organic solvent (dried before use). The mixture was heated to 60–70 °C with constant stirring for 5–6 h, resulting in the formation of a green complex. In low polar solvents (methanol, acetone) it precipitated spontaneously. The latter was filtered off, washed repeatedly with acetone and dried over P_2O_5 for two weeks.

Anal. Calc. (found): C, 27.17 (27.88); H, 5.13 (4.58); N, 27.73 (27.30); Ni, 8.29 (8.48)%.

$[Ni(creat)_3(H_2O)_3] \cdot (NO_3)_2 \cdot H_2O$ (2) (blue)

A total of 0.5 mmol (0.1454 g) $Ni(NO_3)_2 \cdot 6H_2O$ and 2.0 mmol (0.2262 g) creatinine (molar ratio 1:4) was dissolved in 20 cc undried An. The mixture was heated to 60–70 °C with constant stirring for 5–6 h, resulting in the formation of a blue precipitate. The complex was filtered off, washed repeatedly with An and dried over P_2O_5 for 1 h. The complex formed is rather unstable and in several hours its colour changed to green.

Anal. Calc. (found): C, 24.26 (24.62); H, 4.92 (4.73); N, 25.90 (26.28); Ni, 9.88 (10.00)%.

$[Ni(creat)_6](NO_3)_2 \cdot 4H_2O$ (3) (yellow)

This complex was obtained by dissolving 0.5 mmol (0.1454 g) $Ni(NO_3)_2 \cdot 6H_2O$ and 4.0 mmol (0.4525 g) creatinine (molar ratio 1:8) in organic solvent (dried before use) and heating the reaction mixture at 60–70 °C with constant stirring for about 24 h, resulting in the formation of a yellow precipitate**.

---

*Author to whom correspondence should be addressed.

**When a solvent with higher polarity (MAA) was used it was precipitated by adding acetone.

0020-1693/89/$3.50

The latter was filtered off, washed repeatedly with acetone and dried over P_2O_5 for two weeks.

Anal. Calc. (found): C, 30.85 (30.92); H, 5.39 (5.22); N, 30.01 (30.65); Ni, 6.30 (6.74)%.

The composition of the complexes was determined by elemental analysis. Ni content was determined complexometrically in ammonia solution with indicator murexide [8]. The solvents were dried as described in the literature [9].

Apparatus

The electronic, reflectance and IR spectra were recorded on Specord UV–Vis (Carl-Zeiss, Jena), Camag SP 4290 integrator and Perkin-Elmer 983 (CsI disks) spectrometers respectively.

The EPR spectra were obtained on an X-band spectrometer Brucker B-ER 420. The magnetic susceptibility measurements were performed in the 130–350 K range in an argon atmosphere according to the Faraday method and the ESCA measurements on a VIEE-15 spectrometer (energy calibration according to the C 1s line –285.0 eV). Thermogravimetric analysis was performed on a Perkin-Elmer TGS-2C machine.

Results and Discussion

The complexes **1** and **3** are formed consecutively in the course of Ni(II)–creatinine interaction in organic media (in absence of traces of water). Firstly the green complex **1** (λ_{max} = 260; 400; 660; sh ~ 750 nm) was formed. After its isolation from the reaction mixture and drying it proved to be stable for about a month. After this period some changes in the composition and the EPR spectrum of the complex are observed connected most probably with ageing processes. The blue complex **2** is formed under the same conditions as the green one **1**, but only in undried An (containing some traces of water but not more than 0.2%). It precipitates spontaneously from the reaction mixture. The complex proved to be rather unstable and after 2–4 h in the air its colour changed to green. The EPR spectrum of the compound formed is very similar to that of the aged green complex **1**. The yellow complex **3** (λ_{max} = 240; 420; 660 nm) is the final reaction product and proved to be stable for several months.

It should be emphasized that all three complexes are formed only in organic media and their dissolution in water leads to immediate dissociation of the latter: the visible spectra of the corresponding water solutions are indentical with the Ni(II)-aq spectrum. Similarly fast dissociation of $Ni(NH_3)_6^{2+}$ in excess of water is observed and ascribed to the significant kinetic lability of Ni(II) complexes [10].

The visible spectral data of the complexes are typical for octahedral Ni(II) complexes [11, 12]. Taking into account the fact that they are soluble only in the high-polar solvent MAA (D = 100.3 [9]) and insoluble in methanol, acetone, An, it might be assumed that they are charged, e.g. only creatinine and water molecules are included in the inner coordination sphere of the complexes, NO_3^- being in the outer sphere. Both the analytical and visible spectral data indicate the difference in the inner coordination sphere of the complexes. It might be assumed that in **1** two water molecules are included in its inner sphere, while in **3** all four water molecules are in the outer sphere. In order to check this assumption thermogravimetric analysis of the stable **1** and **3** complexes was performed. The data obtained support the assumption for the presence of water molecules in the inner sphere of **1**. The corresponding temperature ranges of dehydration are 83.6–161.5 °C for **1** and 51.3–124.9 °C for **3**. It is evident that in **1** there are water molecules bonded in a stronger way than in **3**, thus supporting the assumption for the presence of two water molecules in the inner coordination sphere of **1**.

In order to obtain more detailed structural information about the complexes studied, magnetochemical, EPR, IR and ESCA measurements were performed. In the temperature range 280–360 K the μ_{eff} values of the three complexes studied are independent of temperature (Fig. 1). These data together with the μ_{eff} values obtained for ambient temperature (~3 BM) are consistent with an octahedral symmetry of the complexes [13]. At temperatures below 240 K a slight temperature dependence of the corresponding μ_{eff} values is observed, which might be due to a change in molecular symmetry. The EPR spectra of the paramagnetic Ni(II) complexes were also recorded in the range 90–300 K. The EPR spectra of **1** and **3** are singlet lines with temperature dependent g values (Table 1), typical for octahedral Ni(II)

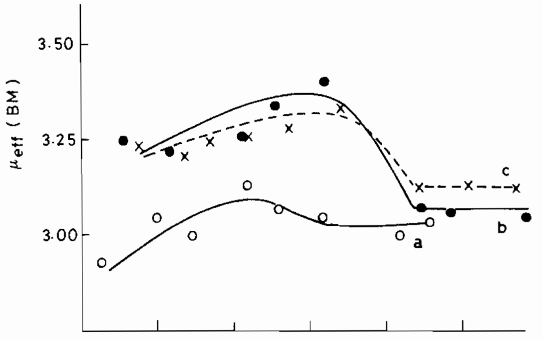


Fig. 1. Dependence of the effective magnetic moment (μ_{eff}) vs. temperature of three complexes: (a) $[Ni(creat)_6](NO_3)_2 \cdot 4H_2O$ (yellow), (b) $[Ni(creat)_4(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (green), (c) $[Ni(creat)_3(H_3O)_3](NO_3)_2 \cdot 2H_2O$ (blue).

TABLE 1. EPR parameters of the Ni(II) complexes

T (K)	1 g (±0.01)	1 ΔH_{pp} (Oe) (±8)	2 g (±0.01)	3 g (±0.01)	3 ΔH_{pp} (Oe) (±8)
100	2.22	292		2.05	117
120	2.22	250	2.11[a]	2.10	
140	2.23	225		2.13	108
150			$g_1 = 2.17$ $g_2 = 2.11$ $g_3 = 2.06$	2.14	
160	2.41		$g_1 = 2.20$ $g_2 = 2.11$ $g_3 = 2.07$		
170	2.41		$g_1 = 2.24$ $g_2 = 2.11$ $g_3 = 2.07$	2.17	258
190			$g_1 = 2.24$ $g_2 = 2.11$ $g_3 = 2.07$	2.18	
250			$g_1 = 2.25$ $g_2 = 2.13$ $g_3 = 2.07$		
290	2.41		$g_1 = 2.27$ $g_2 = 2.16$ $g_3 = 2.05$	2.18	300

[a]Broad singlet line.

complexes [14]. It should be mentioned that below 130–140 K the EPR lines broaden and at 90 K they are not observed at all. A similar effect has been observed for $Ni(NH_3)_6^{2+}$ at temperatures below 76 K and explained by crystal field distortions [14]. The disappearance of the EPR spectrum at $T < 90$ K could be explained in an analogous way with a change in the structure of the complexes 1 and 3 at low temperatures. Another peculiarity of these EPR spectra is their orientation dependence, e.g. variation of the line shape in dependence of the sample orientation in the magnetic field, most probably due to the presence of anisotropic centres in the samples. Similar effects have also been observed for other Ni(II) compounds [15].

On the basis of all the data obtained it might be concluded that the three complexes are octahedral, differing only in their inner coordination sphere. The information obtained for 1 and 3 show the presence of four creatinine and two water molecules in the inner coordination sphere of the green complex 1, while in the yellow complex 3 all six ligands are creatinine molecules, forming a regular octahedron. The EPR spectrum of the blue complex 2 differs significantly from those of 1 and 3 – instead of the singlet, an anisotropic three-component signal is observed (Table 1). Although a more detailed structural investigation on these short-lived intermediate species is hampered, the difference in the visual and EPR spectra again indicates a difference in the inner coordination sphere of 2 in comparison with 1 and 3.

Taking into account the conditions for its formation (presence of traces of water in the solvent used) and the analytical data obtained it might be suggested that these paramagnetic octahedral species contain three water and three creatinine molecules in their inner sphere. The presence of two different types of ligands in the inner sphere of 1 and 2 causes some deviations from the regular octahedral structure of the complexes.

In order to obtain additional information concerning the coordination mode of the ligand, IR and ESCA spectra of the complexes were recorded. The IR spectra of the complexes are very similar to those

TABLE 2. Selected IR data for the free creatinine and its Ni(II) complexes

Complex	$\nu(H_2O)$	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\delta(NH_2)$	$\delta(H_2O)$	$\nu(C{=}O)$	NO_3 vibrations[a] ν_1	 ν_2	 ν_3	 ν_4
Creatinine		3254	3040	1660		1685				
1 (green)	3300br	3380br	3160br	1660	1650	1705 1715 1740sh	1050	850	1360 896	718
2 (blue)	3300br	3370br	3169br	1660	1650	1695 1704 1720sh	1040	858	1358 895	720
3 (yellow)	3300br	3380br	3180br	1665sh	1640	1698 1710 1725sh	1050	850	1355 850	720

[a]Assignment according to Nakamoto [16].

of the monomeric Pt(II) and Pd(II) complexes with creatinine [3, 4]. Selected IR data are represented in Table 2. The IR data obtained show the presence of creatinine in the complexes with its amino form (**I**). Evidently the <C=O group is not involved as far as in the Ni(II) complexes **1**, **2** and **3**; its vibration is observed at higher frequences (above 1700 cm^{-1}) compared with the free ligand. Coordination with the amino group seems unlikely too, although both $-NH_2$ vibration bands are rather broad. Most probably they participate in H bond formation. Analogous results were obtained for Pt(II) and Pd(II) complexes with creatinine [3, 4] where using X-ray diffraction analysis it was proved that coordination is realized only through the endocyclic N atom, the >C=O and $-NH_2$ groups not being involved in the coordination. It might be assumed, therefore, that in the Ni(II) complexes coordination is also realized only through the endocyclic N atom of the ligand.

The data obtained for NO_3^- vibrations are typical for ionic components, thus confirming the presence of NO_3^- in the outer sphere of the complexes.

The ESCA data obtained for **1** and **3** are in agreement with this assumption. The binding energies for Ni 2p (856.8 ± 0.5 eV and 855.8 ± 0.5 eV for **1** and **3** respectively) and N 1s (400.4 ± 0.5 eV and 399.6 ± 0.5 eV for **1** and **3** respectively) are typical for Ni(II) complexes with N-containing ligands [17].

On the basis of all experimental data obtained it might be concluded that in organic media three different types of Ni(II)–creatinine complexes are formed, unstable in water solution. The complexes are paramagnetic with an octahedral structure and differ only in the content of their inner coordination sphere. The IR data indicate coordination through the endocyclic N atom of the ligand. It should be noted that in the course of the reaction a stable radical is formed ($g = 2.0036$) and isolated together with the yellow complex.

References

1 M. Mitewa, P. R. Bontchev and K. Kabassanov, *Polyhedron, 4* (1985) 1159.

2 P. R. Bontchev, M. Mitewa, G. Gencheva, J. Macicek, O. Angelova and V. I. Nefedov, *Proc. 11th Conf. Coord. Chem., Smolenice, CSSR, 1987*, p. 37.

3 M. Mitewa, G. Gencheva, P. R. Bontchev, O. Angelova and J. Macicek, *Polyhedron, 7* (1988) 1273.

4 J. Macicek, O. Angelova, G. Gencheva, M. Mitewa and P. R. Bontchev, *J. Cryst. Spectrosc. Res., 18* (1988) 629.

5 P. R. Bontchev, M. Mitewa and G. Gencheva, *Pure Appl. Chem., 61* (1989) 897.

6 S. Muralidharan, K. S. Nagaraja and M. R. Udupa, *Polyhedron, 3* (1984) 619.

7 S. Muralidharan, K. S. Nagaraja and M. R. Udupa, *Transition Met. Chem., 9* (1984) 218.

8 G. Schwartzenbach and H. Flaschka, *Complexometric Titrations*, Methuen, London, 1969, p. 248.

9 V. Gutman, *Coordination Chemistry in Nonaqueous Medium*, Springer, Vienna, 1968.

10 C. L. Coyle and E. I. Stiefel, in J. R. Lancaster, Jr. (ed.), *The Bioinorganic Chemistry of Nickel*, VCH, New York, 1988, p. 12.

11 L. J. Martin, C. R. Speratti and D. H. Busch, *J. Am. Chem. Soc., 99* (1977) 2968.

12 R. W. Hay, B. Jeragh, S. F. Lincoln and G. H. Searle, *Inorg. Nucl. Chem. Lett., 20* (1981) 2544.

13 B. N. Figgis and J. Lewis, *Progress in Inorganic Chemistry*, Vol. 6, Wiley, New York, 1964, p. 197.

14 B. R. McGarvey, in R. L. Carlin (ed.), *Transition Metal Chemistry*, Vol. 3, M. Dekker, New York, 1966, p. 90.

15 J. S. Lebedev, *Zh. Strukt. Khim., 3* (1962) 151 (in Russian).

16 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 3rd edn., 1978.

17 V. I. Nefedov, *Rontgenoelectronnaja Spectroscopia Khimicheskich Soedinennij*, Khimia, Moscow, 1984.