SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF HETERO METALLIC NITRILOTRIACETATES OF CHROMIUM(III) WITH SOME 3d METALS

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Abstract: Heterometallic complexes of chromium (III) with some 3d metals have been synthesized based on nitrilotriacetic acid (H₄nta), like M(bpy)₂Cr₂(OH)₃(nta)₂·nH₂O, where M = Mn²⁺, Co²⁺, Ni²⁺ and Zn²⁺; bpy = α,α'-bipyridine; n = 8 or 9. Their chemical composition has been determined from the results of the elemental analysis and thermogravimetric study. The coordination modes of the nta⁻⁻ ligand and the type of chemical bonds have been proposed basing on IR spectra.

Keywords: heterometallic, nitrilotriacettes, chromium(III), 3d metals, bipyridine.

Introduction
The scientific and technological interest for new materials by means of complex combinations is explained suggestively having as objective the obtaining of new materials with useful properties. Complex compounds are perspective structures of the M–O(COO¯) bonds. It could be supposed that the appearance of such low values of ∆ν indicates that these groups are bidentate; but if ∆ν <225 cm⁻¹ the bonds are predominantly ionic.

Taking into consideration the high interest for this type of compounds systematic investigations have been proposed to be carried out that will allow the enlarging of the knowledge about heterometallic combinations of chromium (III) with some elements from 3d blocs based on nitrilotriacetic acid (H₄nta).

Results and Discussions
Heterometallic complexes of chromium (III) with some 3d metals have been synthesized based on nitrilotriacetic acid (H₄nta), like M(bpy)₂Cr₂(OH)₃(nta)₂·nH₂O, where M = Mn²⁺ [1], Co²⁺[2], Ni²⁺[3], and Zn²⁺[4], bpy = α,α'-bipyridine; n = 8 or 9 were prepared by exchange reaction between the complex salt Ba[Cr₂(μ-OH)₂(nta)₂]·5H₂O [24] and the respective sulfates on the basis of α,α'-bipyridine. The reactions proceed in aqueous solutions.

The composition of compounds 1-4 was determined from the elemental, thermogravimetric analysis (table 1), IR(table 2) and UV-Vis spectroscopy.

The electronic absorption spectra recorded for the aqueous solutions of compounds 1-4 show 3 bands. Together with the two bands, ν₁(A₂g→T₁g) = 17422 cm⁻¹ (ε = 147.5 1 mol⁻¹ cm⁻¹) and ν₂(A₂g→T₁g) = 24876 cm⁻¹ (ε = 165 l mol⁻¹ cm⁻¹) characteristic for [NO₃⁻] octahedral coordination of Cr(III) with nta⁻⁻ ligand, which are also present in the spectra of the complexes MCr₂(OH)₃(nta)₂·nH₂O described in [25], appears one more signal at ν₃(π→π*) = 31847 cm⁻¹ (ε = 900 l mol⁻¹ cm⁻¹). These parameters confirm the idea that the complexes 1-4 dissociate in solutions but keep the anionic structure unchanged [25, 26].

The analysis of the IR spectra showed that the spectra of the compounds 1-4 are identical having unimportant vibrations of the signals shift. The spectrum of the compound 1 is a little different (table 2).

In the spectra of the compound 1 a very intense signal appears at 1606 cm⁻¹ with a shoulder at 1627 cm⁻¹ and three signals appear at 1386, 1344 and 1312 cm⁻¹ related to ν₂(COO⁻). The differences ∆ν = ν₆(COO⁻) – ν₃(COO⁻) are equal to 220, 262 and 294 cm⁻¹ (for the first signal) and 241, 283 and 315 cm⁻¹ (shoulder signal). According to [27-29] ∆ν differences higher than 250 cm⁻¹ indicate that COO⁻ groups are monodentate, but differences lower than 250 cm⁻¹ indicate that these groups are bidentate; but if ∆ν >225 cm⁻¹ the bonds are predominantly covalent and if ∆ν <225 cm⁻¹ the bonds are predominantly ionic. Taking into consideration these data two coordination modes of the COO⁻ groups are realized in compound 1: two are monodentate having predominantly covalent M–O(COO⁻) bonds and a COO⁻ group is bidentate having intermediary covalent-weak ionic M–O(COO⁻) bond [29]. In the spectra of compounds 2-4 ν₆(COO⁻) signals appear at ca 1605 (2), 1606 (3) and 1605 cm⁻¹ (4), but ν₂(COO⁻) signals appear at 1384 (with shoulder), 1318 cm⁻¹ (2), 1384, 1342, 1318 cm⁻¹ (3) and 1384 (with shoulder), 1319 cm⁻¹ (4). Differences ∆ν = 221, 287 cm⁻¹ (2), 221, 264, 288 cm⁻¹ (3) and 221, 286 cm⁻¹ (4). These ∆ν values are the result of the similar COO⁻ groups coordination of these compounds (2-4) by forming predominantly covalent bonds of the M–O(COO⁻) bonds and of some weak-ionic bonds of the M–O(COO⁻) bonds. It could be supposed that the appearance of such low values ∆ν~221 cm⁻¹ find the explanation in the existence of H···O(COO⁻) bonds, values that cause the diminution of the order of M–O(COO⁻) bonds from covalent to weak-ionic. Hydrogen bonds (intermolecular, three-dimensional) appear in the IR spectra as strong absorption bands with maximum at 3217 cm⁻¹ (1) and 3318 cm⁻¹ (2-4).
The IR spectra of compounds 2-4 showed three bands $\delta_\text{O-C-O}$, $\rho_\text{O-C-O}$ and $\pi_\text{O-C-O}$. This phenomenon is due to the fact that the donor carboxylic groups contribute to the formation of $\text{M-O(}$COO$^-\text{)}$ groups. The fact that a COO$^-$ group of the $\text{nta}^{2-}$ ligand is fixed between two coordination centers leads to the lack of a $\rho_\text{O-C-O}$ signal in the spectra of compound I unlike the series 2-4.

Absorption band $\delta_\text{O-C-O}$, appeared in the IR spectra at 913 (1), 910 (2), 909 (3) and 910 (4) cm$^{-1}$ as a very intense signal. The thermogravimetric analyses of compounds 2-4 showed that these compounds are subject to some thermal transformation while heating (table 1). Dehydration and deaeration processes proceeded over the range 20-180°C in two steps with maximum for the first step ca 70-100°C and for the second step at ca 120-180°C. Dehydration of I occurred in one step with the maximum at 100°C. This different behavior can be explained in the following way: the heating determines the system energy to grow, on the other hand the non-coordinated bipyridine molecules become in such conditions disposed to coordination and substitute the water molecules from the coordination sphere of the Mn atom.

At temperatures over 180-500°C thermal decomposition of the organic parts took place. These processes occurred in one step resulting finely in inorganic residues.

**Experimental Section**

**Synthesis**

\[(\alpha,\alpha^\prime\text{-bipyridyl})\text{-triacyl-manganese}(II)\cdot\text{di-µ-hydroxy-bis-(nitrilotriaceto)dichromium(III)}\]

\[\text{MnSO}_4 \cdot 7\text{H}_2\text{O} \text{ and } 0.32\text{g (2mmol) } \alpha,\alpha\text{-bipyridine were dissolved in 30ml of hot water. A pale yellow solution was obtained. 0.742g (1mmol) crystalline } \text{BaCr}_2(\text{nta})_2(\text{OH})_2 \cdot 5\text{H}_2\text{O, prepared according the source [24], was then added. The mixture was then heated and stirred for an hour at a temperature of 40-50°C. All this gave an intense green-blueish solution, which was filtered, washed with cold water, alcohol and then with acetone and dried at room temperature. Yield 75%. Anal. Found %: Cr 10.20; C 37.39; H 4.65; N 8.05. Calc. for MnCr}_2\text{H}_8\text{N}_4\text{O}_{22} \text{ (1025.67)} \text{ %: Cr 10.14; C 37.47; H 4.52; N 8.19.}

\[(\alpha,\alpha^\prime\text{-bipyridyl})\text{-diaqua-cohalt(II)}\cdot\text{di-µ-hydroxy-bis-(nitrilotriaceto)dichromate(III)}\cdot\text{heptahydrate,}

\[\text{[Co(bpy)}_2\text{(H}_2\text{O})_2\text{]}\text{[Cr}_2\text{(OH)}_2\text{(nta)}_2\text{]}\cdot 7\text{H}_2\text{O (2)}\]

Compound 2 was prepared according to synthesis 1, but the procedure took place in CO$_2$ and N$_2$ environment. After 48h a crystalline blue-violet substance crystallized from the solution, which was then filtered, washed with cold water, alcohol and then with diethyl ether and dried at room temperature. Yield 60%. Anal. Found %: Cr 10.00; C 36.52; H 4.50; N 7.90. Calc. for CoCr$_2$H$_{48}$N$_{48}$O$_{23}$ (1047.68) %: Cr 9.93; C 36.69; H 4.62; N 8.02.

\[(\alpha,\alpha^\prime\text{-bipyridyl})\text{-diaqua-nickel(II)}\cdot\text{di-µ-hydroxy-bis-(nitrilotriaceto)dichromate(III)}\cdot\text{heptahydrate,}

\[\text{[Ni(bpy)}_2\text{(H}_2\text{O})_2\text{]}\text{[Cr}_2\text{(OH)}_2\text{(nta)}_2\text{]}\cdot 7\text{H}_2\text{O (3)}\]

Compound 3 was prepared according to synthesis 1. A crystalline blue-violet substance was obtained. Yield 68%. Anal. Found %: Cr 9.98; C 36.57; H 4.52; N 8.00. Calc. for NiCr$_2$C$_{32}$H$_{68}$N$_{68}$O$_{23}$ (1047.44) %: Cr 9.93; C 36.69; H 4.62; N 8.02.

\[(\alpha,\alpha^\prime\text{-bipyridyl})\text{-diaqua-zinc(II)}\cdot\text{di-µ-hydroxy-bis-(nitrilotriaceto)dichromate(III)}\cdot\text{heptahydrate,}

\[\text{[Zn(bpy)}_2\text{(H}_2\text{O})_2\text{]}\text{[Cr}_2\text{(OH)}_2\text{(nta)}_2\text{]}\cdot 7\text{H}_2\text{O (4)}\]

Compound 4 was prepared according to synthesis 1. A crystalline blue-violet substance was obtained. Yield 62%. Anal. Found %: Cr 9.70; C 36.65; H 4.47; N 7.95. Calc. for ZnCr$_2$C$_{32}$H$_{68}$N$_{68}$O$_{23}$ (1054.14) %: Cr 9.87; C 36.46; H 4.59; N 7.97.

Compounds 1-4 are soluble in water, especially at heating; DMSO, DMF soluble; insoluble in methanol, ethanol, acetone and diethyl ether.

**Table 1. Thermogravimetric analysis**

<table>
<thead>
<tr>
<th>Nr</th>
<th>Complex</th>
<th>Dehydration and deaeration processes, °C</th>
<th>Thermal decomposition, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-nH$_2$O</td>
<td>$\Delta$exp.</td>
</tr>
<tr>
<td>1</td>
<td>Mn(bpy)$_2$Cr$_2$(nta)$_2$(OH)$_2$·8H$_2$O</td>
<td>8</td>
<td>14.5</td>
</tr>
<tr>
<td>2</td>
<td>Co(bpy)$_2$Cr$_2$(nta)$_2$(OH)$_2$·9H$_2$O</td>
<td>4</td>
<td>6.5</td>
</tr>
<tr>
<td>3</td>
<td>Ni(bpy)$_2$Cr$_2$(nta)$_2$(OH)$_2$·9H$_2$O</td>
<td>4</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>Zn(bpy)$_2$Cr$_2$(nta)$_2$(OH)$_2$·9H$_2$O</td>
<td>5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

**Chemical and Physicochemical analyses**

The chemical composition was determined from the general methods of Cr, C, H and N chemical analysis. The water was determined from thermal analysis (table 1).

The thermogravimetric analysis was performed on a Paulik-Paulik-Erday M-102 derivatograph, under air atmosphere, over the temperature range $t_{\text{room}}$ – 800°C, at 2.5°C/min or 5°C/min speed of tests heating. Compounds 1-4 were
analyzed by IR spectroscopy, using tests of tablets form in KBr. IR spectra were recorded on a Perkin Elmer FTIR 1650 spectrometer in the range 4000-400 cm\(^{-1}\) at the Institute of Biology and Molecular Chemistry of Lausanne, Switzerland. Data of IR spectra are given in table 2.

Table 2. IR spectra of the compounds 1-4

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ, cm(^{-1})</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>ν H...OH</td>
<td>3217 broad, intense</td>
<td>3318 broad, intense</td>
<td>3318 broad, intense</td>
<td>3318 broad, intense</td>
</tr>
<tr>
<td>OH</td>
<td>δ Cr–O–H</td>
<td>913 intense</td>
<td>910 intense</td>
<td>909 intense</td>
<td>910 intense</td>
</tr>
<tr>
<td>COO(^-)</td>
<td>ν(_{as}) C–O</td>
<td>1627 (shoulder), 1606 very intense, shoulder</td>
<td>1605 very intense</td>
<td>1606 very intense, shoulder</td>
<td>1605 very intense</td>
</tr>
<tr>
<td></td>
<td>ν(_s) C–O</td>
<td>1386 intense, 1344, medium, 1312 medium, split</td>
<td>1384 with two peaks, intense, shoulder, 1318 medium</td>
<td>1384 with two peaks, intense, shoulder, 1318 medium</td>
<td>1384 intense, shoulder; 1319 medium</td>
</tr>
<tr>
<td></td>
<td>Δν = ν(_{as}) – ν(_s)</td>
<td>220, 241, 262, 283, 294, 315</td>
<td>221, 287</td>
<td>222, 264, 288</td>
<td>221, 286</td>
</tr>
<tr>
<td></td>
<td>δ O–C–O</td>
<td>776, 745, 736 intensely split</td>
<td>748, 736 intense</td>
<td>747, 735 split, two shoulders, intense</td>
<td>736, two shoulders, intense</td>
</tr>
<tr>
<td></td>
<td>ρ(_a) O–C–O</td>
<td>619 shoulder, intense</td>
<td>613 shoulder, intense</td>
<td>613 intense</td>
<td>613 intense</td>
</tr>
<tr>
<td></td>
<td>π O–C–O</td>
<td>528, 514 split, intense</td>
<td>551 intense, 522, 512 split, intense</td>
<td>551 intense, 510, 503 shoulder, very intense</td>
<td>550 intense, 522, 513 very intense</td>
</tr>
<tr>
<td>CN</td>
<td>ν C–N</td>
<td>1107, 1096 split, weak, 1007 shoulder, medium</td>
<td>1094 with two peaks, medium, 1022 medium</td>
<td>1105 with two peaks, medium, 1025 medium</td>
<td>1105 weakly split, 1022 medium</td>
</tr>
<tr>
<td></td>
<td>ν C–H</td>
<td>- weak</td>
<td>2978 weak</td>
<td>- weak</td>
<td>- weak</td>
</tr>
<tr>
<td></td>
<td>δ H–C–H</td>
<td>1461, 1426 medium split</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>ρ(_a) CH(_2)</td>
<td>1271, 1226 medium</td>
<td>1265, split, medium, 1212 medium</td>
<td>1264, split, medium, 1212 medium</td>
<td>1265, split, medium, 1212, medium</td>
</tr>
<tr>
<td></td>
<td>ρ(_t) CH(_2) (gosh)</td>
<td>971 medium</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CC (nta(^3+))</td>
<td>ν C–C</td>
<td>943 medium</td>
<td>947 split, shoulder, medium</td>
<td>947 split, shoulder, medium</td>
<td>947 two shoulders, medium</td>
</tr>
<tr>
<td>CC (bpy)</td>
<td>ν C=C</td>
<td>1492 weak, 1474 medium, 1441 split, medium</td>
<td>1493 medium, 1443 medium, shoulder</td>
<td>1494 medium, 1474 medium, 1444 medium</td>
<td>1493 medium, 1475 medium, 1443 medium, shoulder</td>
</tr>
</tbody>
</table>

Conclusions

1. Four complexes M(bpy)\(_2\)Cr\(_2\)(OH)\(_2\)(nta)\(_2\)·nH\(_2\)O, where M = Mn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\); bpy = \(a,α'\)-bipyridine; n = 8, or 9 have been synthesized. Their chemical composition has been determined from the results of the elemental analysis and thermogravimetric study.

2. According to the data of UV-Vis spectra it has been supposed that complexes 1-4 dissociate in solution but keep the anionic [Cr\(_2\)(OH)\(_2\)(nta)\(_2\)]\(^2-\) structure unchanged.

3. According to the data of the IR spectra two coordination modes of the COO\(^-\) groups are realized in complex 1: two are monodentate having predominantly covalent M–O(COO\(^-\)) bonds and one COO\(^-\) group is bidentate having intermediary covalent-weak ionic M–O(COO\(^-\)) bond. IR spectra of the complexes 2-4 show that the coordination mode of the nta\(^3+\) ligand is identical, M–O(COO\(^-\)) bonds have predominantly covalent character and one weak-ionic character of the M–O(COO\(^-\)). The latter is the result of the existence of H...O(COO\(^-\)) bonds.

4. Thermal analysis of the complexes 1-4 show that at temperatures over 180°C they loose the hydration and coordination water molecules, but at temperatures over 180-500°C the thermal decomposition of the organic parts takes place.
Acknowledgments
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References