

SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF HETEROMETALLIC 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 (H_3nta), like $M(bpy)_2Cr_2(OH)_2(nta)_2 \cdot nH_2O$, where $M = Mn^{2+}$, Co^{2+} , Ni^{2+} and Zn^{2+} ; $bpy = \alpha, \alpha'$ -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^{3-} ligand and the type of chemical bonds have been proposed basing on IR spectra.

Keywords: heterometallic, nitrilotriacetates, 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 precursors for the synthesis of materials with catalytic [1-3], electric [4-6] and magnetic [7-9] properties. In this sense chromium (III) compounds came to be promising in the design of magnetic materials [10-17]. Thus, depending on basic ligands, the bridging and contraions ones from outer sphere, compounds with ferro- and antiferromagnetic [7-23] properties are obtained.

Taking into consideration the high interest for this type of compounds systemic 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 (H_3nta).

Results and Discussions

Heterometallic complexes of chromium (III) with some 3d metals have been synthesized based on nitrilotriacetic acid (H_3nta), like $M(bpy)_2Cr_2(OH)_2(nta)_2 \cdot nH_2O$, where $M = Mn^{2+}$ [1], Co^{2+} [2], Ni^{2+} [3], and Zn^{2+} [4], $bpy = \alpha, \alpha'$ -bipyridine; $n = 8$ or 9 were prepared by exchange reaction between the complex salt $Ba[Cr_2(\mu-OH)_2(nta)_2] \cdot 5H_2O$ [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, $\nu_1(^4A_{2g} \rightarrow ^4T_{2g}) = 17422 \text{ cm}^{-1}$ ($\epsilon = 147.5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and $\nu_2(^4A_{2g} \rightarrow ^4T_{1g}) = 24876 \text{ cm}^{-1}$ ($\epsilon = 165 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) characteristic for $\{NO_5\}$ octahedral coordination for Cr(III) with nta^{3-} ligand, which are also present in the spectra of the complexes $MCr_2(OH)_2(nta)_2 \cdot nH_2O$ described in [25], appears one more signal at $\nu_3(\pi \rightarrow \pi^*) = 31847 \text{ cm}^{-1}$ ($\epsilon = 900 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). 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 spectrum 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 $\nu_s(COO^-)$. The differences $\Delta\nu = \nu_{as}(COO^-) - \nu_s(COO^-)$ 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] $\Delta\nu$ 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 $\Delta\nu > 225 \text{ cm}^{-1}$ the bonds are predominantly covalent and if $\Delta\nu < 225 \text{ cm}^{-1}$ 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** $\nu_{as}(COO^-)$ signals appear at *ca* 1605 (**2**), 1606 (**3**) and 1605 cm^{-1} (**4**), but $\nu_s(COO^-)$ 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 $\Delta\nu = 221$, 287 cm^{-1} (**2**), 221 , 264 , 288 cm^{-1} (**3**) and 221 , 286 cm^{-1} (**4**). These $\Delta\nu$ 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 $\Delta\nu \sim 221 \text{ cm}^{-1}$ find the explanation in the existence of $H \dots O(COO^-)$ 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 $\delta_{(O-C-O)}$, $\rho_{\omega(O-C-O)}$ and $\pi_{(O-C-O)}$. This phenomenon is due to the fact that the donor carboxylic groups contribute to the formation of $M-O(COO^-)$ groups. The fact that a COO^- group of the nta^{3-} ligand is fixed between two coordination centers leads to the lack of a $\rho_{\omega(O-C-O)}$ signal in the spectra of compound **1** unlike the series **2-4**.

Absorption band $\delta_{(Cr-O-H)}$ 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 subdued to some thermal transformation while heating (table 1). Dehydration and deaquation 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 **1** 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

*[(α, α' -bipyridyl)-triaqua-manganese(II)-{di- μ -hydroxy-bis-(nitriлотriacetato)dichromium(III)}]-(α, α' -bipyridylate)-pentahydrate, $[Mn(H_2O)_3(bpy)Cr_2(OH)_2(nta)_2] \cdot (bpy) \cdot 5H_2O$ (**1**)*

0,246g (1mmol) $MnSO_4 \cdot 7H_2O$ and 0,32g (2mmol) α, α' -bipyridine were dissolved in 30ml of hot water. A pale yellow solution was obtained. 0,742g (1mmol) crystalline $BaCr_2(nta)_2(OH)_2 \cdot 5H_2O$, 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-bluish solution, which was filtered and concentrated by evaporation at a temperature of 40-50°C to a 20ml volume. Within 24 hours a green-bluish crystalline substance precipitated from the solution, which was then 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 $MnCr_2C_{32}H_{46}N_6O_{22}$ (**1025.67**) %: Cr 10.14; C 37.47; H 4.52; N 8.19.

*[Di-(α, α' -bipyridyl)-diaqua-cobalt(II)][di- μ -hydroxy-bis-(nitriлотriacetato)dichromate(III)] heptahydrate, $[Co(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2] \cdot 7H_2O$ (**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 $CoCr_2C_{32}H_{48}N_6O_{23}$ (**1047.68**) %: Cr 9.93; C 36.69; H 4.62; N 8.02.

*[Di-(α, α' -bipyridyl)-diaqua-nickel(II)][di- μ -hydroxy-bis-(nitriлотriacetato)dichromate(III)] heptahydrate, $[Ni(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2] \cdot 7H_2O$ (**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 $NiCr_2C_{32}H_{48}N_6O_{23}$ (**1047.44**) %: Cr 9.93; C 36.69; H 4.62; N 8.02.

*[Di-(α, α' -bipyridyl)-diaqua-zinc(II)][di- μ -hydroxy-bis-(nitriлотriacetato)dichromate(III)] heptahydrate, $[Zn(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2] \cdot 7H_2O$ (**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 $ZnCr_2C_{32}H_{48}N_6O_{23}$ (**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

Nr	Complex	Dehydration and deaquation processes, °C						Thermal decomposition, °C	
		-nH ₂ O	Δ_{exp}	Δ_{calc}	Start	Max.	Fin.	Start	Fin.
1	$Mn(bpy)_2Cr_2(nta)_2(OH)_2 \cdot 8H_2O$	8	14.5	14.05	50	100	120	220	470
2	$Co(bpy)_2Cr_2(nta)_2(OH)_2 \cdot 9H_2O$	4	6.5	6.88	50	100	120	240	460
		5	9.0	8.60	120	150	180		
3	$Ni(bpy)_2Cr_2(nta)_2(OH)_2 \cdot 9H_2O$	4	6.5	6.88	40	80	100	180	470
		5	9.0	8.60	100	140	180		
4	$Zn(bpy)_2Cr_2(nta)_2(OH)_2 \cdot 9H_2O$	5	8.5	8.54	20	70	100	180	430
		4	7.0	6.84	100	120	180		

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 $t_{room} - 800^\circ C$, 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

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

Conclusions

- Four complexes $\text{M}(\text{bpy})_2\text{Cr}_2(\text{OH})_2(\text{nta})_2 \cdot n\text{H}_2\text{O}$, where $\text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$ and Zn^{2+} ; *bpy* = α, 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.
- According to the data of UV-Vis spectra it has been supposed that complexes **1-4** dissociate in solution but keep the anionic $[\text{Cr}_2(\text{OH})_2(\text{nta})_2]^{2-}$ structure unchanged.
- 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.
- 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.

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References

- [1] Gulea A., et al. / 52ND World Exhibition of Innovation Research and New Technology, Brussels, Eureka, 11-16/11/2003, Book of Abstracts, sec. 7, p. 76.
- [2] Gibson V. et al. // J. Chem. Soc., Dalton Trans., 2002, 4017-4023.
- [3] Ruck R. Jacobsen E. // J. Amer. Chem. Soc., 2002, 124, 12, 2882-2883.
- [4] V. Tapcov, A. Gulea, V. Stavila. / Moldavian Patent MD2146. BOPI, no. 4, 2003.
- [5] Gulea A., et al. / Moldavian Patent MD1559. BOPI no. 11, 2000.
- [6] Myung S.-T., et al. // J. Power Sources, 2003, 119-121, 211-215.
- [7] Kahn O. *“Molecular Magnetism”*, New York: VCH, 1993. 380p.
- [8] Coronado E., et al. // J. Solid State Chemistry, 2001, 159, 391-402.
- [9] Hua Xi., et al. // New J. Chem., 2001, 25, 875-878.
- [10] Andruh M., et al. // Inorg. Chim. Acta, 1996, 251, 309-317.
- [11] Stanica N., et al. // Polihedron, 1998, 17, 10, 1787-1789.
- [12] Muñoz C., et al. // J. Chem. Soc., Dalton Trans., 1998, 3125-3131.
- [13] Marinescu G., et al. // New J. Chem., 2000, 24, 527-536.
- [14] Lescouëzec R., et al. // New J. Chem., 2001, 25, 1224-1235.
- [15] Costisor O., et al. // Inorg. Chim. Acta, 2001, 324, 352-358.
- [16] Marinescu G., et al. // Inorg. Chim. Acta, 2002, 336, 46-54.
- [17] Chiozzone R., et al. // Inorg. Chem., 1999, 38, 4745-4752.
- [18] Fujihara Ta., Fuyuhiko Ak., Kaizaki Su. // Inorg. Chim. Acta, 1998, 278, 15-23.
- [19] Ross S., et al. // Inorg. Chim. Acta, 2002, 339, 71-76.
- [20] Green Ch., et al. // Inorg. Chim. Acta, 1990, 176, 87-93.
- [21] Fujihara Ta., Fuyuhiko Ak., Kaizaki Su. // J. Chem. Soc., Dalton Trans., 1995, 1813-1821.
- [22] Ni-ya K., et al. // Bull. Chem. Soc. Japan., 2001, 74, 1891-1897.
- [23] Kawamura Ya., et al. // Inorg. Chim. Acta, 2004, 357, 2437-2440.
- [24] Victor Ciornea // Anal. Științ. USM, ser. “Șt. chim.-biol.”, 2004, 425-431.
- [25] Novitchi G., et al. // Eur. J. Inorg. Chem., 2005, 929-937.
- [26] V. Ciornea, et al. / XXII Межд. Чугаевская конф. по коорд. химии, 20-24 июня 2005, г. Кишинёв. Тезисы докладов. с. 226.
- [27] Накамото К. *“ИК-спектры и спектры КР неорганических и комплексных соединений”* М., Мир, 1991; сс. 259-271.
- [28] G. B. Deacon, R. J. Phillips // Coord. Chem. Rev., 1980, 33, 227.
- [29] *„Координационная химия редкоземельных элементов”* М., Изд-во Моск. Ун-та, 1979; сс. 76-101.