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Coordination Compounds of Co(II), Ni(II) and Cu(II) with Capric Acid Hydrazide

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The reaction of aquo-ethanolic solutions of Co(II), Ni(II) and Cu(II) salts and ethanolic solution of capric acid hydrazide (L) yielded paramagnetic, high-spin bis- and tris(ligand) chelate complexes. The tris(ligand) complexes, $[ML_3]X_2 \cdot nH_2O$ [M = Co(II), Ni(II); $X = NO_3^-$, ClO_4^-, $1/2 SO_4^{2-}$], have an octahedral structure formed on account of the bidentate (NO) coordination of three neutral hydrazide molecules. In the bis(ligand) complexes, $ML_2(NCS)_2$ [M = Co(II), Ni(II)] and $CuL_2X_2 \cdot nH_2O$ ($X = NO_3^-$, ClO_4^- and $1/2 SO_4^{2-}$), the oxoanions and NCS^- take also part in coordination. The complexes have been characterized by elemental analysis, IR spectra, magnetic measurements, molar conductivity and TG analysis.

[Keywords: Co(II), Ni(II) *and* Cu(II) *complexes; Capric acid hydrazide as ligand; Physico-chemical characterization]*

Caprinsäurehydrazid-Komplexe von Co(II), Ni(II) *und* Cu(II)

Durch die Reaktion von wäßrig-ethanolischen Lösungen von Co(II)-, Ni(II)- und Cu(II)-Salzen mit einer ethanolischen Lösung von Caprinsäurehydrazid (L) wurden paramagnetische high-spin Bis- und Tris-Ligand-Chelatkomplexe erhalten. Tris-Ligand-Komplexe des Typs $[ML_3X_2 \cdot nH_2O$ [M = Co(II), Ni(II); $X = NO_3^-$, ClO_4^-, $1/2 SO_4^{2-}$], die eine oktaedrische Struktur besitzen, entstehen durch die Koordination von drei neutralen zweizähnigen (NO)-Hydrazidmolekülen. Bei den Bis-Ligand-Komplexen $ML_2(NCS)_2$ [M = Co(II), Ni(II)], sowie bei den Bis-Ligand-Komplexen $CuL_2X_2 \cdot nH_2O$ ($X = NO_3^-$, ClO_4^-, $1/2 SO_4^{2-}$) nehmen bei der Koordination außer Hydrazid auch die Säurereste teil. Die Komplexe wurden durch Elementaranalyse, IR-Spektren, magnetische Messungen, molare Leitfähigkeit und TG-Analysen charakterisiert.

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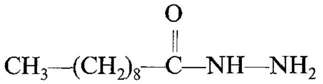
Introduction

A number of metal complexes with hydrazides of different aliphatic acids, including those with caprilic and capronic acid [1–5] have been prepared and thoroughly investigated. Since there have been no data in the literature on the synthesis of complexes of 3 d elements with capric acid hydrazide,



$$CH_3{-}(CH_2)_8{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}NH_2 \qquad (L)$$

the objective of this work was to study the reaction conditions for preparation of Co(II), Ni(II) and Cu(II) complexes with this ligand, as well as their physico-chemical properties, with the aim to find out the possible effect of the aliphatic chain length on the characteristics of the synthesized complexes.

Results and Discussion

In the reaction of warm ethanolic solutions of $MX_2 \cdot 6\,H_2O$ [M = Co(II), Ni(II); $X = NO_3^-$, ClO_4^-, $1/2\,SO_4^{2-}$] and warm ethanolic solution of capric acid hydrazide (L) in the mole ratio 1 : 3, the tris(ligand) chelate complexes of the general formula $[ML_3]X_2 \cdot nH_2O$ are obtained. Their composition and elemental analysis, as well as of the other complexes, have been presented in Table 1. In contrast to Co(II) and Ni(II), the Cu(II) ion gives (in the presence of the same oxoanions) only bis(ligand) complex, independant of the mole ratio of Cu(II) and L. This indicates that the nature of the central ion affects the composition of the resulting complex. The effect of the nature of inorganic anions on the type of complex formed can be illustrated in the case of thiocyanate. This ligand forms with Co(II) and Ni(II) only bis(ligand) complexes, regardless on the mole ratio, which is certainly due to a more pronounced coordination affinity of the NCS group compared to the oxoanions. On the other hand, the analogous complex, $CuL_2(NCS)_2$, could not be isolated because of reduction of Cu(II), occurring even in the reaction of the ethanolic solution of CuL_2X_2 ($X = NO_3^-$, ClO_4^-) and NH_4NCS.

All the obtained complexes are microcrystalline substances, sparingly soluble in water and more in methanol and ethanol, except of the sulphate complexes and $CuL_2(NO_3)_2 \cdot H_2O$, which also show a low solubility in the latter solvents.

An analysis of the IR spectra of the ligand and complexes (recorded in KBr) shows that $\nu(NH_2, NH)$, $\nu(C{=}O)$, as well as $\delta(NH_2)$ for the complexes are shifted towards lower energies if compared to the

Table 1. *Elemental analysis of* Co(II), Ni(II) *and* Cu(II) *complexes with capric acid hydrazide (L); (calculated values in parentheses)*

Complex	*M*	C	H	N
$[CoL_3](NO_3)_2$	7.85 (7.94)	49.04 (48.57)	8.81 (8.97)	15.16 (15.10)
$[CoL_3](ClO_4)_2 \cdot 2H_2O$	6.74 (6.91)	42.63 (42.25)	8.65 (8.27)	9.98 (9.86)
$[CoL_3]SO_4 \cdot 2H_2O$	7.98 (7.85)	47.97 (48.05)	9.73 (9.41)	11.05 (11.21)
$[CoL_2(NCS)_2]$	10.54 (10.76)	48.56 (48.25)	8.38 (8.10)	15.27 (15.34)
$[NiL_3](NO_3)_2$	7.65 (7.92)	48.13 (48.58)	9.21 (8.97)	14.87 (15.11)
$[NiL_3](ClO_4)_2 \cdot H_2O$	7.01 (7.06)	43.85 (43.17)	8.36 (8.21)	10.20 (10.07)
$[NiL_3]SO_4 \cdot 2H_2O$	7.61 (7.83)	47.72 (48.06)	9.67 (9.41)	11.51 (11.21)
$[NiL_2(NCS)_2]$	10.64 (10.72)	47.88 (48.26)	7.82 (8.10)	15.27 (15.35)
$[CuL_2(NO_3)]NO_3$	11.24 (11.34)	43.22 (42.88)	8.17 (7.92)	15.18 (15.00)
$[CuL_2(ClO_4)_2] \cdot H_2O$	9.52 (9.73)	37.11 (36.78)	7.43 (7.10)	8.69 (8.58)
$[CuL_2(SO_4)H_2O]$	11.62 (11.54)	43.59 (43.66)	8.19 (8.43)	10.11 (10.18)

corresponding bands in the ligand spectrum (Table 2). However, these shifts, especially for the $\nu(C=O)$ band, are far more evident in the spectra recorded in $CHCl_3$, where this band appears at higher energies. This suggests the existence of relatively strong hydrogen bonds in the ligand in its crystalline form [6].

On the basis of the above evidences it can be concluded that the title ligand, like most hydrazides studied, is coordinated as a bidentate one in its keto-form via the nitrogen and oxygen of the $>C=O$ and $—NH_2$ group, respectively.

The values for effective magnetic moments of the complexes are characteristic of high-spin states of the metal ions involved. In addition, in the case of Co(II) and Ni(II) this suggests the presence of an octahedral coordination [7], which is in the case of tris(ligand) complexes accomplished on account of a bidentate (NO) coordination of three neutral hydrazide molecules. The conclusion is supported by $\nu_{as}(NO_3)$, $\nu_{as}(ClO_4)$ and $\nu_{as}(SO_4)$ bands in the IR spectra (Table 2), the position and shape of which prove that the oxoanions do not act as ligands [7, 8]. Further support is given by the molar conductivities measured in methanolic solutions (Tab. 3), which are characteristic of the electrolyte of 2 : 1 type [9].

The octahedral structure of the bis(ligand) complexes can be explained by participation in coordination, apart from two neutral molecules of the bidentate hydrazide, of NCS^- and oxoanions and water molecules. Therefore, in the IR spectra of NCS complexes (Table 2) the very strong band at about 2 100 cm^{-1} is split in two, which can be ascribed to $\nu(C=N)$ vibration of NCS in *cis*-position [4]. The molar conductivities also

Table 2. *Selected IR bands (cm^{-1}) of* Co(II), Ni(II), *and* Cu(II) *complexes with capric acid hydrazide (L)*

Compounds	$\nu(H_2O)$	$\nu(NH)$, $\nu(NH_2)$	$\nu(C{=}O)$	$\delta(NH_2)$	ν(Anion)
Ligand		3 460*, 3 340* 3 340, 3 320 3 200, 3 060	1 680* 1 655	1 635* 1 635	
$[CoL_3](NO_3)_2$		3 200 3 060	1 650	1 620	1 380
$[CoL_3](ClO_4)_2 \cdot 2\,H_2O$	3 500	3 320, 3 200 3 040	1 650	1 620	1 100
$[CoL_3]SO_4 \cdot 2\,H_2O$	3 500	3 280, 3 240 3 180, 3 060	1 650	1 610	1 100
$[CoL_2(NCS)_2]$		3 260, 3 240 3 200, 3 060	1 655	1 610	2 110, 2 090
$[NiL_3](NO_3)_2$		3 280, 3 200 3 050	1 650	1 620	1 380
$[NiL_3](ClO_4)_2 \cdot H_2O$	3 500	3 320, 3 200 3 060	1 650	1 620	1 120
$[NiL_3]SO_4 \cdot 2\,H_2O$	3 440	3 250, 3 200 3 060	1 655	1 620	1 100
$[NiL_2(NCS)_2]$		3 250, 3 200 3 050	1 650	1 610	2 100, 2 115
$[CuL_2(NO_3)]NO_3$		3 280, 3 160 3 040	1 640	1 600	1 380, 1 335 830
$[CuL_2(ClO_4)_2] \cdot H_2O$	3 500	3 220, 3 180 3 040	1 645	1 505	1 150, 1 120, 1 100
$[CuL_2(SO_4)H_2O]$	3 440	3 220, 3 160 3 060	1 670	1 640	1 145, 1 120, 1 110 1 100

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* In $CHCl_3$

Table 3. *Some physiochemical characteristics of the* Co(II), Ni(II) *and* Cu(II) *complexes with capric acid hydrazide (L)*

Complex	Colour	$\mu_{\mathrm{eff}\,(\mathrm{BM})}$	$\lambda_{\mathrm{M}\,(\mathrm{S\,cm^2\,mol^{-1}})}$
$[\mathrm{Co}L_3](\mathrm{NO_3})_2$	light-pink	4.86	129.6
$[\mathrm{Co}L_3](\mathrm{ClO_4})\cdot 2\,\mathrm{H_2O}$	light-pink	4.84	162.9
$[\mathrm{Co}L_3]\mathrm{SO_4}\cdot 2\,\mathrm{H_2O}$	light-pink	4.95	insoluble
$[\mathrm{Co}L_2(\mathrm{NCS})_2]$	red-pink	5.03	72.7
$[\mathrm{Ni}L_3](\mathrm{NO_3})_2$	light-blue	3.12	135.8
$[\mathrm{Ni}L_3](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$	light-blue	3.18	158.3
$[\mathrm{Ni}L_3]\mathrm{SO_4}\cdot 2\,\mathrm{H_2O}$	grey-blue	3.08	insoluble
$[\mathrm{Ni}L_2(\mathrm{NCS})_2]$	grey-blue	3.20	83.7
$[\mathrm{Cu}L_2(\mathrm{NO_3})]\mathrm{NO_3}$	grey-blue	2.06	insoluble
$[\mathrm{Cu}L_2(\mathrm{ClO_4})_2]\cdot\mathrm{H_2O}$	light-blue	1.97	158.8
$[\mathrm{Cu}L_2(\mathrm{SO_4})\mathrm{H_2O}]$	blue	1.93	insoluble

indicate that at least one NCS group is coordinated. Somewhat higher conductivity values than expected for a non-electrolyte can be explained by nucleophilic and solvation properties of the solvent employed.

In contrast to tris(ligand) complexes of Ni(II) and Co(II) containing non-coordinated $\mathrm{SO_4^{2-}}$, $\mathrm{NO_3^-}$ and $\mathrm{ClO_4^-}$, the corresponding Cu(II) complexes have these oxoanions as ligands, which can be concluded on the basis of IR spectra. Thus, three distinctly separated band of a relatively high intensity (Fig. 1) are present in the spectrum of $\mathrm{Cu}L_2\mathrm{SO_4}\cdot\mathrm{H_2O}$ at about 1 100 $\mathrm{cm^{-1}}$, and absent in the case of $\mathrm{Cu}L_2(\mathrm{NO_3})_2$, suggesting that sulphate is involved in the coordination [7, 8]. The IR spectrum of the sulphate complex differs also from those for all other complexes with respect to the position of the $\nu(\mathrm{C{=}O})$ and $\delta(\mathrm{NH_2})$ bands. As seen from Table 2, these bands are shifted towards higher energies compared to their positions in the spectra, not only of the complexes, but also of the ligand in crystalline state. Since these bands in the spectrum of the complex are observed at lower energies than in the case of the ligand in solution, it might be assumed that the ligand is still bidentate, but its metal-ligand bonds are very weak.

Thermogravimetric analysis of this and other sulphate complexes showed that water loss occurred at a higher temperature (180 °C) than in the case of tris(ligand) sulphate complexes of Co(II) and Ni(II) (150 and 145 °C, respectively), which suggests that in the case of $\mathrm{Cu}L_2\mathrm{SO_4}\cdot\mathrm{H_2O}$ water also takes part in coordination.

In the IR spectrum of $\mathrm{Cu}L_2(\mathrm{NO_3})_2$, recorded both in KBr and hexachlorobutadiene, there are bands characteristic of both coordinated and non-coordinated $\mathrm{NO_3}$ group (Table 2). It should be noticed that the band corresponding to the coordinated nitrate observed at higher energies (1 530–1 480 cm^{-1}) [8], could not be identified because of the interference of a band of the ligand itself.

The IR spectrum for $CuL_2(ClO_4)_2 \cdot H_2O$, (Fig. 2) indicates that it also takes part in coordination. As seen from Fig. 2, the shape of the $\nu_{as}(ClO_4)$ band of $NiL_3(ClO_4)_2$, which is taken as an example of the outer sphere ClO_4 group, differs from that of the copper complex. In the latter case the band tends to split, which can be explained in terms of the coordination effect of the parchlorate ion [7, 8]. However, it is true that such a shape of the $\nu_{as}(ClO_4)$ band might be also due to the presence of hydrogen bonds, as well as to the crystal lattice effect. On the other hand, the molar conductivity of this complex, which does practically not differ from the values for the perchlorate tris(ligand) complexes of Co(II) and Ni(II) (Table 3), is contradictory to the assumption of a coordination of the perchlorate group. But having in mind that metal-perchlorate bonds are

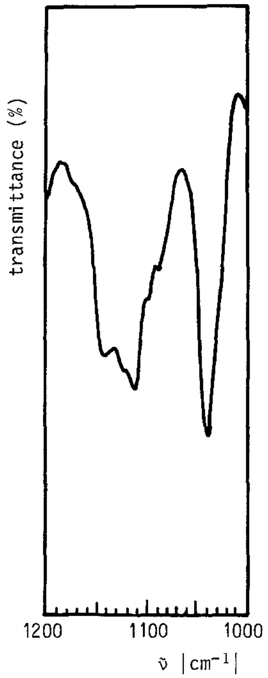

Fig. 1. IR spektrum of $[CuL_2(SO_4)(H_2O)]$ in the region of SO_4 vibrations (in KBr)

very weak, the value for the molar conductivity should not be considered as a pertinent fact, since it gives no information on the nature of bands in the crystal.

By comparing our findings with the literature data on complexes of the same 3d-elements with hydrazides of other aliphatic acids [1–5] it can be concluded that the metal ions under consideration form (in the presence of the same inorganic anions) complexes of an analogous type. Therefore the aliphatic chain length of the hydrazides has no effect on the type of complex. A similar ligand behaviour of these hydrazides is also evident from the formation of complexes of Co(II), Ni(II) and Cu(II), having the same (high spin) electronic configuration.

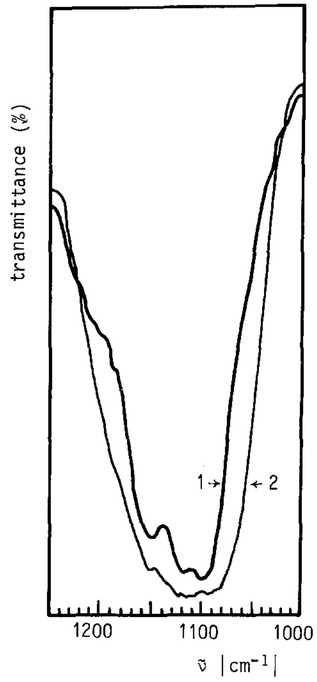

Fig. 2. IR spektrum in the region of ClO_4 vibrations (in KBr) of $[CuL_2(ClO_4)_2] \cdot H_2O$ (*1*) and $[NiL_3](ClO_4)_2 \cdot H_2O$ (*2*)

These results can be explained by similar properties of all hydrazides as a class of ligands which are coordinated in their keto-form, employing the same (NO) donor atoms.

Experimental

The ligand was synthesized according to a general procedure [10].

The complexes of $[ML_3]X_2\cdot n\mathrm{H_2O}$ [M = Co(II), Ni(II); $X = \mathrm{NO_3^-}$, $\mathrm{ClO_4^-}$, $1/2\,\mathrm{SO_4^{2-}}$] and $ML_2X_2\cdot n\mathrm{H_2O}$ [M = Co(II), Ni(II); X = NCS; M = Cu(II); $X = \mathrm{NO_3^-}$, $\mathrm{ClO_4^-}$, $1/2\,\mathrm{SO_4^{2-}}$] type were prepared by mixing warm concentrated aquo-ethanolic solutions of the hydrazide and the corresponding salt in a mole ratio $M:L = 1:3$ and $M:L = 1:2$, respectively. The reacting mixtures in the case of sulphate, nitrate and thiocyanate complexes were left at room temperature for 3 hours, and in the case of perchlorate complexes for about 10 hours. After that, the crystalline precipitates were filtered off and washed with ethanol (in the case of sulphate complex with water, too) and ether. Yield: 60–80%.

The air-dry substances were used for all analyses. The metal ion contents were determined by the complexometric method [11], while C, H and N were determined by standard methods in the Department of Instrumental Analysis, Faculty of Sciences, Belgrade. The water content in the sulphate complexes was determined by the thermogravimetric method on a Paulik-Paulik-Erdey derivatograph.

IR spectra were recorded in KBr using a Perkin-Elmer 457 instrument. Magnetic susceptibility was measured by *Faraday*'s method at room temperature and using $\mathrm{Hg[Co(NCS)_4]}$ as a standard. The molar conductivity of $1\cdot 10^{-3}\,\mathrm{mol\,dm^{-3}}$ methanolic solutions was measured at room temperature using a conductivity meter MA 5962 Iskra, Kranj.

References

[1] *Kharitonov YuYa, Machkhosvili RI* (1971) Zh Neorg Khimii 16: 924

[2] *Kharitonov YuYa, Machkhosvili RI, Metreveli DP* (1976) Koordinatsionnaya khimiya 2: 131

[3] *Mostafa MM, Nicholls D* (1981) Inorg Chim Acta 51: 35

[4] *Machakhoshvili RI, Shalamberidze TV, Shchelokov RN* (1982) Zh Neorg Khim 27: 1226

[5] *Machkhoshvili RI, Shalamberidze TV, Shchelokov RN* (1982) Zh Neorg Khim 27: 1725

[6] *Grekov AP, Veselov VYa* (1979) Fizicheskaya khimiya gidrazina, Kiev: Naukova dumka

[7] *Cotton FA, Wilkinson G* (1971) Advanced inorganic chemistry. Wiley-Interscience, New York

[8] *Nakamoto K* (1970) Infrared spectra of inorganic and coordination compounds. Wiley Interscience, New York

[9] *Geary WJ* (1964) Coord Chem Rev 51: 285

[10] *Grekov AP* (1966) Organicheskaya khimiya gidrazina. Tekhnika: Kiev

[11] *Schwarzenbach G, Flaschka H* (1965) Die komplexometrische Titration. Ferdinand Enke, Stuttgart