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Note

Synthesis and Properties of Coordination Compounds of Co(II) and Ni(II) with 3,4,5-Trimethoxybenzoylhydrazine

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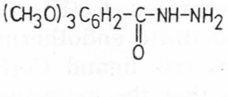
The synthesis of Co(II) and Ni(II) complexes with 3,4,5-trimethoxybenzoylhydrazine HL of the formula $M(HL)nX_2 \cdot mH_2O$ are reported. The complexes were prepared by the reaction of HL with metal(II) nitrate, acetate, sulphate, and chloride. The magnetic properties, infrared and electronic spectra show that metal(II) is 6-coordinated, HL being bound as a bidentate (ON) ligand.

INTRODUCTION

The aroylhydrazine and many hydrazine derivatives have been reported to inhibit many reactions catalyzed by pyridoxal-5-phosphate as coenzyme[1,2]. Many substituted acid hydrazides have been used for the treatment of psychotic and psychoneurotic conditions[3]. The antitubercular activity has been attributed to their ability to form chelates with Cu(II) ions[4].

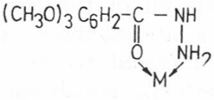
The coordination chemistry of aroylhydrazines has been the object of extensive studies[5-8], which have revealed that these compounds react with metal(II) ions to give cationic bis- or tris ligand chelates in which the central metal ion coordinated via nitrogen of the primary amino group and the oxygen atom of the carbonyl group. This fact has been confirmed by X-ray determinations[9-11].

It might be expected that this organic ligand 3,4,5-trimethoxybenzoylhydrazine (I), would behave similarly to other aroylhydrazines. By analogy, this molecule may acts as a bidentate ligand with NO coordination sites with formation of chelating rings of type (II).



$(CH_3O)_3C_6H_2-\underset{\underset{O}{\|}}{C}-NH-NH_2$

(I)



(II)

EXPERIMENTAL

Preparation of 3,4,5-Trimethoxybenzoylhydrazine (HL)[12]

The 3,4,5-trimethoxybenzoylhydrazine was prepared by the reaction of hydrazine hydrate with methyl-3,4,5-trimethoxybenzoate in equal ratio. The ethanol reaction mixture was refluxed for 3 hrs. On cooling, the precipitated compound was filtered, washed with ethanol and then dried under vacuum. The 3,4,5-trimethoxybenzoylhydrazine was a colourless substance, $T_m = 431$ K.

Preparation of Ni(II) Complexes, $Ni(HL)_nX_2 \cdot mH_2O$

A hot water solution of Ni(II) salts, nitrates, acetates, sulphates and chlorides (0.01 mol) was treated with a hot solution of HL in ethanol (0.02 and 0.03 mole, respectively). The reaction mixture was refluxed for 30 min. On cooling, the precipitated metal complex was filtered, washed with hot ethanol and then dried in a vacuum desiccator.

Preparation of Co(II) Complexes, $Co(HL)_nX_2 \cdot mH_2O$

With the exception of anhydrous cationic bis ligand Co(II) complexes, $Co(HL)_2Cl_2$, this type complexes were also prepared in a similar way from the reaction of Co(II) salts with HL. In boiling ethanol (without the presence of water), the reaction of $CoCl_2$ with HL yielded the corresponding anhydrous complex of the formula $Co(HL)_2Cl_2$.

Infrared spectra were made with Perkin-Elmer 580 spectrophotometer with KBr discs.

Electronic spectra were made with Photoacustic spectrometer GILFORD R-1500.

Magnetic measurements were taken at room temperature by the Faraday method, using Hg $Co(NCS)_4$ as calibrant. Conventional diamagnetic corrections were made by employing Pascal's constants[13].

The thermogravimetric analyses were made with thermoanalysis apparatus Netzsch, Geratebau GmbH Selb, with Al_2O_3 as standard substance.

The molar conductance of DMF solution (10^{-3} mol dm^{-3}) at 298 K was obtained by conductometer type MA 5962 Iskra-Kranj.

RESULTS AND DISCUSSION

Synthesis of the commercially unavailable 3,4,5-trimethoxybenzoylhydrazine HL was the starting point of our investigation. This organic compound was further used as a ligand for synthesis of coordination compounds with Co(II) and Ni(II) salts. The complexes of HL were obtained from ethanol solution of ligand and aqueous solutions of the corresponding metal nitrate, acetate, sulphate and chloride. Based on the elementary analyses and thermogravimetry of the water content (Tables I and II), the synthesized complexes can be represented by the formula $M(HL)_nX_2 \cdot mH_2O$

$$(M = Co(II),\ Ni(II);\quad HL = (CH_3O)_3\text{—}C_6H_2\text{—}CONHNH_2 \quad n = 2,\ 3;$$

$$X = NO_3,\ CH_3COO,\ 1/2\ SO_4,\ Cl;\quad m = O,\ 3,\ 4)$$

The cobalt complexes were of a pink colour while the nickel complexes were blue. All the complexes of cobalt and nickel were insoluble in water, slightly soluble in ethanol and methanol and quite soluble in DMF.

With the exception of the tris ligand complex, $Co(HL)_3(NO_3)_2 \cdot 4H_2O$, differential thermal analyses show only one definite endothermic effect (region 373—433 K). The thermal treatment of this tris ligand Co(II) complex gave two endothermic effects, which can indicate that the molecules of water leave the complex in two steps (Figure 1).

TABLE I

Analytical Data and T$_m$ *of Co(II) Complexes*

Complexes	M/%	C/%	H/%	N/%	S/%	Cl/%	H$_2$O/%	T_m/K
Co(HL)$_3$(NO$_3$)$_2\cdot$4H$_2$O	6.55	37.99	5.31	12.26			8.17	511
(Co C$_{30}$H$_{50}$N$_8$O$_{22}$)	(6.31)*	(38.59)	(5.39)	(12.00)			(7.72)	
Co(HL)$_2$(CH$_3$COO)$_2$	9.77	45.11	5.51	9.17				477
(Co C$_{24}$H$_{34}$N$_4$O$_{12}$)	(9.36)	(45.79)	5.44	(8.90)				
Co(HL)$_2$(SO$_4\cdot$4H$_2$O	8.80	35.98	5.11	9.05	4.54		10.70	over
(Co C$_{20}$H$_{36}$N$_4$O$_{16}$S)	(8.67)	(35.35)	(5.34)	(8.24)	(4.71)		(10.60)	523
Co(HL)$_3$Cl$_2\cdot$4H$_2$O	6.69	41.17	5.22	10.09		8.56	8.68	465
(Co C$_{30}$H$_{50}$N$_6$O$_{16}$Cl$_2$)	(6.69)	(40.91)	(5.72)	(9.54)		(8.05)	(8.18)	
Co(HL)$_2$Cl$_2$	9.76	40.99	4.71	9.45		12.66		482
(Co C$_{20}$H$_{28}$N$_4$O$_8$Cl$_2$)	(10.12)	(41.25)	(4.84)	(9.62)		(12.17)		

* The values in brackets are calculated.

TABLE II

Analytical Data and T$_m$ *of Ni(II) Complexes*

Complexes	M/%	C/%	H/%	N/%	S/%	Cl/%	H$_2$O/%	T_m/K
Ni(HL)$_3$(NO$_3$)$_2\cdot$3H$_2$O	6.48	39.05	5.02	12.52			5.82	527
(Ni C$_{30}$H$_{48}$N$_8$O$_{21}$)	(6.41)*	(39.35)	(5.28)	(12.24)			(5.78)	
Ni(HL)$_2$(CH$_3$COO)$_2$	9.03	45.10	5.29	0.33				505
(Ni C$_{24}$H$_{34}$N$_4$O$_{12}$)	(9.33)	(45.80)	(5.44)	(8.90)				
Ni(HL)$_2$SO$_4\cdot$4H$_2$O	8.88	34.94	5.57	9.00	4.86		10.60	over
(Ni C$_{20}$H$_{36}$N$_4$O$_{16}$S)	(8.64)	(35.36)	(5.33)	(8.24)	(4.72)		(10.60)	523
Ni(HL)$_2$Cl$_2\cdot$4H$_2$O	9.13	36.08	5.73	9.11		11.02	11.57	476
(Ni C$_{20}$H$_{36}$N$_4$O$_{12}$Cl$_2$)	(8.97)	(36.72)	(5.54)	(8.56)		(10.84)	(11.01)	

* The values in brackets are calculated.

The prepared 3,4,5-trimethoxybenzoylhydrazine and the corresponding Co(II) and Ni(II) complexes were characterized by infrared and electronic spectra and magnetic measurements.

In the spectrum of HL three bands are observed in the stretching NH region. The middle one is probably due to the ν (NH) vibration and the other two have been assigned to the ν_{as} (NH$_2$) and ν_s (NH$_2$) vibrations, respectively (Table III).

The bending δ (NH$_2$) vibration and the Amide I vibration are coupled and form two bands.

In the NH and OH stretching region, broad bands with several submaxima are observed with Co(II) and Ni(II) complexes. Amide I vibration appears in all the complexes, with the exception of the acetates which are overlapped by the ν_{as} (COO) vibration. In the range of Amid II vibration, a low intensity band is observed while in the region of Amid III vibration an intensive band appears. These changes are probably the result of the coordination of ligand HL through carbonyl oxygen and nitrogen of the amino group with formation of chelating five membered rings.

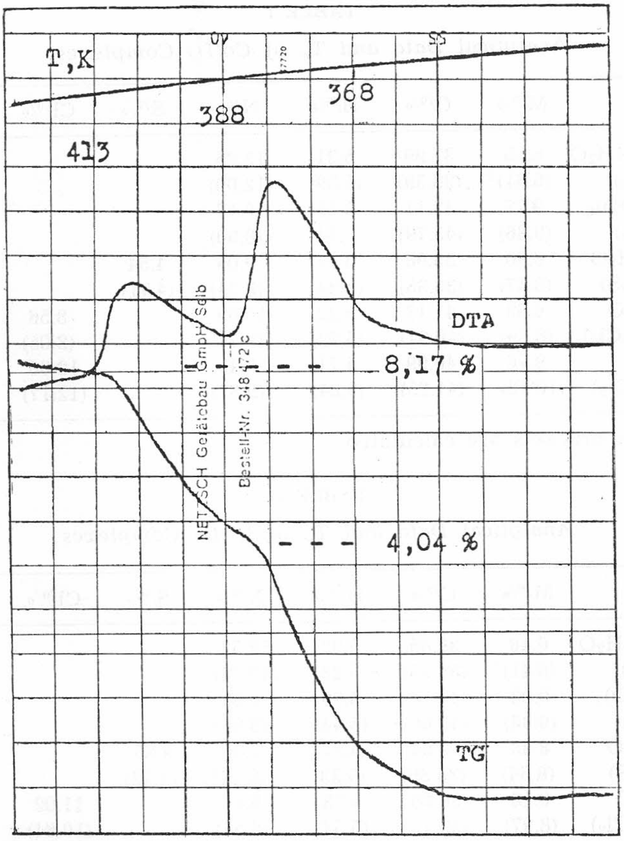


Figure 1. The thermogram of $Co(HL)_3(NO_3)_2 \cdot 4H_2O$

The presence of polyatomic anions is manifested by the appearance of bands in the corresponding regions[14] (Table III).

Magnetic measurements showed that these are high-spin complexes with effective magnetic moments (Table IV), typical of pseudooctahedral stereochemistry[15]. Magnetic properties of high-spin octahedral Co(II) complexes are governed by the orbitally degenerate ground term ^4T_1g, and these are experimentally found to be in the range 4.57—4.80 μ_B.

Electronic spectra show that they consist of a band in the near infrared region, which is assigned to the lowest energy transition $^4T_1g \rightarrow {}^4T_2g$, and a band in the visible region which is assigned to the $^4T_1g \rightarrow {}^4T_1g(P)$ transition (Table V).

Nickel(II) complexes show magnetic moments in the range 3.11—3.28 μ_B typical of six-coordinate complexes which are high-spin, having either regular or distorted octahedral stereochemistry. The electronic spectra of these complexes with the bands in the region containing $^3A_2g \rightarrow {}^3T_2g$ and $^3A_2g \rightarrow {}^3T_1g(F)$ transition are in good agreement with their stereochemistry (Table VI).

TABLE III

Infrared Spectral Data (cm^{-1}) for Isolated Compounds

Compounds	ν(NH), ν(OH) $\nu_{as}(NH_2)$, $\nu_s(NH_2)$	Amide I $\delta(NH_2)$	Amide II Amide III	
(HL)	3335m 3380m 3300s	1650m 1610m	1545s 1350s	
$Co(HL)_3(NO_3)_2 \cdot 4H_2O$	3400w 3305m 3250m	1642s 1600m	1540m 1355s	ν(NO) 1385s
$Co(HL)_2(CH_3COO)_2$	3205s 3095m 3003w	ν(COO) 1670m 1612w	1548sh 1358s	
$Co(HL)_2SO_4 \cdot 4H_2O$	3500sh 3400m 3200m	1667w 1640w 1615m	1550sh 1358s	ν(SO) 1128 1115s 1072
$Co(HL_3Cl_2 \cdot 4H_2O$	3585w 3500m 3400m 3260w 3200s	1663s 1650m 1610s	1540s 1358s	
$Co(HL)_2Cl_2$	3200s	1645s 1600w	1540s 1350s	
$Ni(HL)_3(NO_3)_2 \cdot 3H_2O$	3415m 3250m 3170m	1640m 1605w	1545s 1350s	ν(NO) 1380s
$Ni(HL)_2(CH_3COO)_2$	3200s 3070m	ν(COO) 1670m 1615w	1543s	
$Ni(HL)_2SO_4 \cdot 4H_2O$	3400m 3250m 3150m	1640m 1605sh	1548s 1350s	ν(SO) 1125s
$Ni(HL)_2Cl_2 \cdot 4H_2O$	3400 m 3150m 3060m	1640 1600sh	1535s 1350s	

TABLE IV

Magnetic Measurements Data and Molar Conductivity of the Complexes

Complexes	Colour	μ_{eff}/μ_B	λ S cm^2 mol^{-1}
$Co(HL)_3(NO_3)_2 \cdot 4H_2O$	pink	4.57	168.00
$Co(HL)_2(CH_3COO)_2$	pink	4.66	7.09
$Co(HL)_2SO_4 \cdot 4H_2O$	pink	4.58	29.80
$Co(HL)_3Cl_2 \cdot 4H_2O$	pink	4.67	33.80
$Co(HL)_2Cl_2$	pink	4.80	18.50
$Ni(HL)_3(NO_3)_2 \cdot 3H_2O$	blue	3.11	138.00
$Ni(HL)_2(CH_3COO)_2$	blue	3.28	7.13
$Ni(HL)_2SO_4 \cdot 4H_2O$	blue	3.26	12.30
$Ni(HL)_2Cl_2 \cdot 4H_2O$	blue	3.13	23.50

TABLE V

Electronic Spectral Data (cm^{-1}) for Co(II) Complexes

Complexes	$^4T_1g \rightarrow ^4T_1g(P)$	$^4T_1g \rightarrow ^4T_2g$
$Co(HL)_2Cl_2$	19 047m	10 131s
$Co(HL)_3(NO_3)_2 \cdot 4H_2O$	18 348m	10 152s
$Co(HL)_3Cl_2 \cdot 4H_2O$	18 181m	10 101s
$Co(HL)_2SO_4 \cdot 4H_2O$	18 181w 20 408m	10 152s
$Co(HL)_2(CH_3COO)_2$	20 000m	10 121s

TABLE VI

Electronic Spectral Data (cm^{-1}) for Ni(II) Complexes

Complexes	$^3A_2g \rightarrow ^3T_1g$	$^3A_2g \rightarrow ^3T_2g$
$Ni(HL)_2(CH_3COO)_2$	16 181m	10 152s
$Ni(HL)_3(NO_3)_2 \cdot 3H_2O$	16 129w	10 204s
$Ni(HL)_2SO_4 \cdot 4H_2O$	16 000m	10 101s
$Ni(HL)_2Cl_2 \cdot 4H_2O$	16 666m	10 277s

The colour of the solid substance, as well as the observed bands in the electronic spectra, point out to the predicted octahedral symmetry[16]. The values for the molar conductivity obtained in DMF determine the nitrate complexes as ternary electrolytes, while the other complexes can be considered as slight and non-electrolytes[17]. The solution of Co(II) complexes in DMF shows a change in colour from pink to blue. This change is the result of the formation of the tetrahedral species in the solution, and the presence of octahedral ⇌ tetrahedral equilibria.

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SAŽETAK

Sinteza i svojstva koordinacionih spojeva 3,4,5-trimetoksibenzoilhidrazina sa prelaznim metalima

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Sintetizovani su i proučavana su svojstva Co(II) i Ni(II) kompleksa sa 3,4,5-trimetoksibenzoilhidrazinom HL. Nađeno je da ti spojevi imaju opću formulu M(HL)n)X·mH_2O. Kompleksi su dobiveni reakcijom liganda (HL) sa metal(II)-solima (nitrat, acetat, sulfat i klorid).

Magnetna svojstva, infracrveni i elektronski spektri kompleksa pokazuju da je metal(II) 6-koordiniran, pri čemu HL djeluje kao bidentatni (ON) ligand.