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# Synthesis and Structural Studies of Co(II) and Ni(II) Complexes of Glutaric- and Adipic Dihydrazides

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Glutaric dihydrazide (*GDH*) and adipic dihydrazide (*ADH*) have been found to react with Co(II) chloride and Ni(II) chloride and nitrate in ethanolic solution to form complexes of the general empirical compositions $MLCl_2$, $ML_2Cl_2$ and $[NiL_2(H_2O)_2](NO_3)_2$ where $M =$ Co(II), Ni(II) and $L = GDH$, *ADH*. Tetrahedral geometry has been proposed for 1:1 complexes of Co(II) and octahedral geometry for the remaining complexes based on measurements of molar conductance, magnetic susceptibility, electronic and ir spectra.

*[Keywords: Co(II) complexes; Conductance; Ni(II) complexes; Susceptibility]*

*Synthese und Struktur von Co(II)- und Ni(II)-Komplexen von Glutarsäure- und Adipinsäuredihydraziden*

Glutarsäuredihydrazid (*GDH*) und Adipinsäuredihydrazid (*ADH*) bilden mit Co(II)-Chlorid und Ni(II)-Chlorid bzw. -Nitrat in ethanolischer Lösung Komplexe der generellen Zusammensetzungen $MLCl_2$, $ML_2Cl_2$ und $[NiL(H_2O)_2](NO_3)_2$, mit $M =$ Co(II), Ni(II) und $L = GDH$, *ADH*. Für 1:1-Komplexe von Co(II) wird eine tetragonale Geometrie, für alle anderen Komplexe eine oktaedrische Geometrie vorgeschlagen. Die Basis dazu lieferten Messungen der molaren Leitfähigkeit, der magnetischen Suszeptibilität und der UV- bzw. IR-Spektren.

## Introduction

In continuation of our earlier work[1] on VO(IV) complexes of dihydrazides, we report here the results of our studies on Co(II) and Ni(II) complexes of *GDH* and *ADH*.

## Materials and Methods

Metal chlorides and nitrate used in this study were of BDH(LR) grade. The ligands were synthesized as described elsewhere[1].

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Table 1. *Analytical data*[a] *and effective magnetic moments of GDH and ADH complexes*

| Complex | Colour | Metal | Chloride | Hydrazine | Loss of water | Molar conductance at $10^{-3}M$ ($\Omega^{-1}$cm$^2$ mol$^{-1}$ | $\mu_{\text{eff.}}$ $(\mu_B)^c$ |
|---|---|---|---|---|---|---|---|
| Ni($GDH$)$Cl_2$ | light green | 20.20<br>(20.26) | 24.45<br>(24.51) | 22.10<br>(22.09) | — | 1.72 | 3.00 |
| Ni($GDH$)$_2Cl_2$ | blue | 13.00<br>(13.05) | 15.85<br>(15.79) | 28.30<br>(28.46) | — | 1.48 | 3.24 |
| [Ni($GDH$)$_2(H_2O)_2$] $(NO_3)_2$ | blue | 10.92<br>(10.90) | — | 25.90[b]<br>(25.98) | 6.70<br>(6.68) | — | 3.24 |
| Co($GDH$)$Cl_2$ | blue | 20.50<br>(20.32) | 24.54<br>(24.49) | 21.80<br>(22.08) | — | 2.96 | 4.71 |
| Co($GDH$)$_2Cl_2$ | pink | 13.04<br>(13.10) | 15.65<br>(15.79) | 28.48<br>(28.44) | — | 1.92 | 4.92 |
| Ni($ADH$)$Cl_2$ | light green | 19.30<br>(19.33) | 23.20<br>(23.38) | 21.15<br>(21.08) | — | 2.36 | 2.92 |
| Ni($ADH$)$_2Cl_2$ | blue | 12.35<br>(12.29) | 14.90<br>(14.87) | 26.64<br>(26.80) | — | 6.51 | 3.19 |
| [Ni($ADH$)$_2(H_2O)_2$] $(NO_3)_2$ | blue | 10.35<br>(10.36) | — | 24.54[b]<br>(24.71) | 6.30<br>(6.35) | — | 3.20 |
| Co($ADH$)$Cl_2$ | blue | 19.54<br>(19.39) | 23.40<br>(23.36) | 21.20<br>(21.06) | — | 2.71 | 4.66 |
| Co($ADH$)$_2Cl_2$ | pink | 12.45<br>(12.33) | 14.80<br>(14.86) | 26.58<br>(26.80) | — | 2.96 | 5.04 |

[a] Calculated values are given in parenthesis (%).
[b] Values for nitrogen (hydrazine + nitrate).
[c] Bohr magnetons.

Table 2. *Important infrared spectral bands and assignments*

| Complex | Amide I | β $(NH_2)$ | Amide II | ν (N—N) | ν $(NO_3^-)$ | $f_r$ $(H_2O)$ | ν (*M*—O) | ν (*M*—N) | ν (*M*—Cl) |
|---|---|---|---|---|---|---|---|---|---|
| *GDH*[a] | 1625 s | 1600 w | 1525 m | 896 w | — | — | — | — | — |
| *GDH*[b] | 1680 s | 1600 w | 1525 m | 896 w | — | — | — | — | — |
| $\mathrm{Ni}(\mathit{GDH})\mathrm{Cl}_2$ | 1650 s | 1575 s | 1520 m | 930 w | — | — | 345 m | 230 w | 300 m |
| $\mathrm{Ni}(\mathit{GDH})_2\mathrm{Cl}_2$ | 1630 s | 1600 s | 1520 m | 896 w | — | — | 350 w | — | 280 w |
| $[\mathrm{Ni}(\mathit{GDH})_2(\mathrm{H_2O})_2](\mathrm{NO_3})_2$ | 1640 s | 1600 s | 1520 m | 900 w | 1380 s, 825 m | 760 w | 355 w | — | — |
| $\mathrm{Co}(\mathit{GDH})\mathrm{Cl}_2$ | 1650 s | 1600 s | 1520 m | 896 w | — | — | 340 m | — | 295 m |
| $\mathrm{Co}(\mathit{GDH})_2\mathrm{Cl}_2$ | 1640 s | 1600 s | 1520 m | 896 w | — | — | 345 w | — | 280 m |
| *ADH*[a] | 1630 s | 1600 sh | 1530 s | 896 w | — | — | — | — | — |
| *ADH*[b] | 1680 s | 1600 sh | 1530 s | 896 w | — | — | — | — | — |
| $\mathrm{Ni}(\mathit{ADH})\mathrm{Cl}_2$ | 1630 s | 1590 s | 1520 m | 950 w | — | — | 350 m | 255 w | 290 w |
| $\mathrm{Ni}(\mathit{ADH})_2\mathrm{Cl}_2$ | 1630 s | 1600 s | 1525 m | 900 w | — | — | 340 s | — | 270 s |
| $[\mathrm{Ni}(\mathit{ADH})_2(\mathrm{H_2O})_2](\mathrm{NO_3})_2$ | 1650 s | 1600 s | 1525 m | 900 w | 1380 s, 825 m | 750 w | 390 m | — | — |
| $\mathrm{Co}(\mathit{ADH})\mathrm{Cl}_2$ | 1645 s | 1590 s | 1525 m | 905 w | — | — | 390 m | — | 355 m |
| $\mathrm{Co}(\mathit{ADH})_2\mathrm{Cl}_2$ | 1640 s | 1605 s | 1525 m | 896 w | — | — | 435 w | — | 375 w |

[a] Nujol.

[b] Acetonitrile solution.

### Synthesis and Analysis of the Complexes

The complexes were prepared by mixing together hot ethanolic solutions of the metal chloride/nitrate and the ligand in about 1:1 and/or 1:2 molar ratios. $ML_2Cl_2$ and $[NiL_2(H_2O)_2](NO_3)_2$ complexes precipitated immediately while the precipitation of $MLCl_2$ complexes was affected by adding ether to the reaction mixture. The complexes thus obtained were filtered, washed with ethanol, ether and dried at room temperature.

Metals were analyzed employing standard procedures[2] after destroying the organic part at first with a mixture of nitric and hydrochloric acid and then with concentrated sulphuric acid. Hydrazine was estimated[2] by $KIO_3$ after submitting the complexes to acid hydrolysis for ~4 h and chloride was estimated as silver chloride. The analytical data are given in Table 1.

### Physical Measurements

Experimental details pertaining to the molar conductance, magnetic susceptibility, electronic and ir spectral measurements were the same as described in our earlier paper[1]. Magnetic moments and molar conductances of the complexes are included in the Table 1, while ir spectral bands and their assignments are listed in Table 2.

## Results and Discussion

*GDH* and *ADH* form complexes of two different stoichiometries viz., $MLCl_2$ and $ML_2Cl_2$ with metal chlorides, as indicated by analytical data (Table 1). All the comlexes are insoluble in water and common organic solvents but chloride complexes are slightly soluble in cold/hot *DMSO*. All the complexes do not melt up to 250 °C while 1:1 and 1:2 *GDH* complexes of Co(II) melt at 235 °C and 248 °C respectively.

The loss of water molecules in the temperature range of 140–160 °C, the presence of a band in the 750–760 $cm^{-1}$ region (characteristic for coordinated water) and its absence in the corresponding anhydrous complexes show that water molecules are coordinated[3].

The values of molar conductance of the chloride complexes in *DMSO* at 0.001 *M* concentration lie in the range 1.48–6.51 $\Omega^{-1}\,cm^2\,mol^{-1}$, suggesting their nonionic[4] nature. The magnetic moments show that 1:1 cobalt(II) complexes are tetrahedral while all other complexes have spin-free octahedral geometry[5].

### Electronic Spectra

Two bands appearing at 35,710 ($\epsilon_{max.} = 22{,}500$ for *GDH*, 28,000 for *ADH*) and 33,330 ($\epsilon_{max.} = 14{,}500$ for *GDH*, 17,500 for *ADH*) $cm^{-1}$ in the uv spectra of *GDH* and *ADH* in ethanol are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of $>C=O$ and $-NH_2$ groups respectively. The shift of the first band to the high energy side[6] (40,820-44,440 $cm^{-1}$) and disappearance of the second band in all the complexes indicates coordination of the ligands through $>C=O$ and/or —$NH_2$ groups.

The 1:2 Co(II) complexes yield three bands in ~9,302, 14,810-15,380 and 20,000-20,410 $cm^{-1}$ regions due to $^4T_{1g}(F) \rightarrow {^4T_{2g}}(F)$ ($\nu_1$), $^4A_{2g}$ $(F)$ ($\nu_2$) and $^4T_{1g}(P)$ ($\nu_3$) transitions respectively while 1:1 complexes of Co(II) give two bands in 4,760-4,820 and 14,290-14,560 $cm^{-1}$ regions assigned to $^4A_{2g} \rightarrow {^4T_{1g}}$ $(F)$ ($\nu_2$) and $^4T_{1g}$ $(P)$ ($\nu_3$) transitions respectively supporting the octahedral geometry[7] for the former complexes and tetrahedral geometry[8] for the latter complexes as inferred from the magnetic measurements discussed above. Three *d-d* transition bands observed in 9,302-10,530, 14,810-17,040 and 25,000-28,570 $cm^{-1}$ regions in all the Ni(II) complexes attributed to $^3A_{2g}$ $(F) \rightarrow {^3T_{2g}}$ $(F)$ ($\nu_1$), $^3T_{1g}$ $(F)$ ($\nu_2$) and $^3T_{1g}$ $(P)$ ($\nu_3$) transitions respectively are characteristic of octahedral[9] coordination around Ni(II). The octahedral geometry for Ni(II) complexes is further supported by a $\nu_2/\nu_1$ ratio[10] in the range of 1.55-1.64.

The various ligand field parameters such as $10Dq$, $B'$, $\beta$, $\beta^\circ$ and *LFSE* have been evaluated[11] and were found to lie in the ranges 2,715-10,530 $cm^{-1}$, 723-946 $cm^{-1}$, 0.709-0.896, 10.42-29.07% and 38.81-150.50 kJ $mol^{-1}$ respectively. A place between water and ammonia for the ligands is suggested in the spectrochemical series on the basis of $10\,Dq$ values of the complexes.

## *Infrared Spectra*

The bonding sites of the ligands have been determined by a careful comparsion of the ir spectra of the complexes with those of the ligands in acetonitrile solution. Since the spectra of the complexes are rather broad in the NH stretching frequency region it is difficult to draw any conclusion regarding coordination of the ligands through —NH- or —$NH_2$ groups.

The bands appearing in the solution spectra of the ligands at 1,680, 1,600, 1,525, 896 $cm^{-1}$ and at 1,680, 1,600, 1,530, 896 $cm^{-1}$ are attributed[1] to amide I, $\beta(NH_2)$ or $NH_2$ deformation, amide II and $\nu$(N—N) modes respectively. The occurrence of only one band due to amide I and amide II bands at lower frequency in the spectra of the complexes compared to those of the parent ligands shows the coordination of the ligands through both of the symmetrical carbonyl groups in all 1:1 and 1:2 complexes.

A negative shift (5-10 $cm^{-1}$) in $\beta$ ($NH_2$) and a positive shift (34-54 $cm^{-1}$) in $\nu$ (N—N) modes in the spectra of 1:1 complexes of Ni(II) indicate that in addition to the two carbonyl oxygens, both —$NH_2$

groups are also involved in bonding in these complexes. The appearance of bands due to above modes practically at the same position in the spectra of the ligands and all 1:2 and 1:1 Co(II) complexes shows that the nitrogens of —$NH_2$ groups do not take part in bonding in these complexes.

The presence of a strong band centred at 1,380 $cm^{-1}$ and a medium intensity band at 825 $cm^{-1}$ in nitrate complexes shows that $NO_3^-$ is ionically[12] bonded in these complexes.

The nonligand bands appearing in 340-435, 225-310 and 270-375 $cm^{-1}$ regions in the spectra of the complexes may be tentatively assigned to $\nu(M—O)$[13], $\nu(M—N)$[13] and $\nu(M—Cl)$[14] modes respectively.

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