Complexes of Some 3d-Metal Salts with N,N-Dimethylhydrazide of 4-Nitrobenzoic Acid

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Abstract—The $[M(HL)_2(H_2O)_2]X_2$ complexes were synthesized (M = Mn(II), Co(II), Ni(II), Cu(II), Zn; X =

CH₃COO⁻, Cl⁻, BF₄⁻) that incorporate bidentately coordinated molecules of *N*,*N*-dimethylhydrazide of 4-nitrobenzoic acid (HL). The latter molecules chelate the metal atom through the carbonyl O atom and the N atom of dimethylamino group. The square-planar complexes of Cu and Ni with deprotonated form of a ligand with composition ML₂ were also isolated. The synthesized complexes were studied by IR, electronic and EPR spectroscopies, and by cyclic voltammetry.

The problem of recovery of extremely toxic 1,1dimethylhydrazine stimulated an interest in the studies of the processes that can be used to convert it into ecologically friendly products. One of these processes consists in its transformation into hydrazides of carboxylic acids and their metal complexes, which are well known as the biologically active compounds [1, 2]. The coordination chemistry of hydrazide complexes has been considered in many publications, but the majority of studies in this field deal with the unsubstituted hydrazide complexes containing a terminal primary amino group [3–8]. However, the derivatives of nonasymmetric N,N-dimethylhydrazine as ligands in the coordination compounds are poorly studied.

Previously, we described the synthesis and study of the metal complexes with *N*,*N*-dimethylhydrazides of 2,4-dichlorophenoxyacetic and α -(2-methyl-4-chlorophenoxy)propionic acids that have pronounced herbicide properties. It was shown that in the reactions with the metal salts, these hydrazides form complexes only with a neutral amide form of the ligand (**I**). As the result of the steric effect of methyl groups at the donor N atom, these complexes have rather low stability [9].

Attempts to produce stable complexes with the deprotonated imido form (\mathbf{II}) of these hydrazides by increasing the solution pH led, as a rule, to the hydrolysis of the metal salts.



The capability of hydrazides to give different compounds is known to depend on many factors. An important role is played by the nature of organic radical R that can affect the prototropic conversions in hydrazides of acids. The organic radicals that exhibit a strong negative induction effect bring about the redistribution of electronic density in the hydrazide molecule:



As the result, the mobile H atom of the NH group becomes ionized, which is necessary for the intermolecular tautomeric conversion [7].

In our further studies of complexation processes, we synthesized *N*,*N*-dimethylhydrazide of 4-nitrobenzoic acid (HL) containing organic radical with the negative induction effect.

EXPERIMENTAL

N,*N*-dimethylhydrazide of 4-nitrobenzoic acid was obtained by condensation of nonasymmetric dimethyl-hydrazine with *para*-nitrobenzoyl chloride:



The ¹H NMR spectrum of HL (δ, ppm): 2.59 (6H, –CH₃); 7.98 (2H, H₁); 8.28 (2H, H₂); 9.71 (1H, NH–), mp 151–152°C.

Compound	Color	Content (found/calcd), %			
		М	N	Cl	
$[Mn(HL)_2(H_2O)_2]Ac_2$	Yellow	8.63/8.76	13.65/13.40		
$[Ni(HL)_2(H_2O)_2]Ac_2$	Green	9.38/9.30	13.57/13.32		
[Ni(HL) ₂ (H ₂ O) ₂]Cl ₂	Green	10.10/10.05	14.49/14.39	12.30/12.14	
[Ni(HL) ₂ (H ₂ O) ₂](BF ₄) ₂	Light blue	8.67/8.55	12.32/12.24		
$[Co(HL)_2(H_2O)_2]Ac_2$	Pink	9.27/9.33	13.50/13.31		
$[Co(HL)_2(H_2O)_2]Cl_2$	Pink	10.17/10.09	14.43/14.39	12.03/12.13	
$[Zn(HL)_2(H_2O)_2]Ac_2$	White	10.13/10.25	13.11/13.18		
$[Zn(HL)_2Cl_2]$	White	11.67/11.79	15.42/15.15	12.60/12.78	
[CuL ₂]	Red	13.11/13.24	17.38/17.51		
[NiL ₂]	Yellow	12.15/12.36	17.83/17.69		

 Table 1. Results of elemental analysis of the synthesized hydrazide metal complexes

The metal complexes were prepared by pouring together the alcohol solution of hydrazide (2 mmol) and a hot alcohol (or water–alcohol) solution of a metal salt (1 mmol). The metal salts used included the chlorides, acetates, and tetrafluoroborates of Mn, Co, Ni, Cu, and Zn. The reaction mixture was heated at constant stirring for 10 min on a water bath and was allowed to stand for a day. The obtained crystals were filtered off.

The composition and structure of the synthesized complexes with the HL derivatives were established by the chemical analysis (Table 1) and by the electronic, IR, and EPR spectroscopies. The electronic absorption and the diffuse reflection spectra were recorded on a Specord M40 spectrophotometer in the range of 400–900 nm. IR spectra were taken on a Specord M80 spectrophotometer in the range of 400–4000 cm⁻¹ (with KBr pellets). The EPR spectra were recorded on a mini PS 100.X EPR spectrometer (ADANI) at 293 and 77 K and 9480 MHz.

The acid–base equilibrium in the solutions of *N*,*N*-dimethylhydrazides were studied by pH-metric titration using automated MOLSPIN titration system with a combined glass–calomel microelectrode calibrated against the HNO₃ solutions at 25°C. The concentration of hydrazide was 3×10^{-3} mol/l. All calculations were performed with SUPERQUAD program.

Electrochemical measurements were carried out with a three-electrode cell with a platinum working microelectrode (10 μ M in diameter), a platinum plate auxiliary electrode (with 1 cm² surface area), and silver-chloride reference electrode connected to the solution under consideration through an electrolytic bridge containing a supporting electrolyte. The ferrocenium/ferrocene (Fc⁺/Fc) redox couple (with the redox potential 0.47 V relative to the reference electrode used) served as an internal standard. All potentials presented below are given with respect to the Fc⁺/Fc couple.

A solution of tetraethylammonium tetrafluoroborate in acetonitrile (with the salt concentrationa 0.1 mol/l) was used as a supporting electrolyte. The salt was preliminarily dried in vacuum at 100° C in order to remove moisture, and then acetonitrile that was purified and dried beforehand was added in a stream of argon. The potential sweep was controlled with a PI 50.1 potentiostat, the current was measured with a high-resistance V 7-45 voltmeter, and voltammograms were recorded on a XY Recorder A3.

RESULTS AND DISCUSSION

Hydrazides dissociate according to the acid mechanism as follows:

$$R \longrightarrow {}^{O}_{NH-N(CH_3)_2} \Longrightarrow R \longrightarrow {}^{O^-}_{N-N(CH_3)_2} + H^+.$$

The pH-metric study of this process for HL and for the previously described hydrazides gave the following values of dissociation constants

Hydrazide
$$pK_a$$

$$\begin{array}{c} Cl \longrightarrow O \\ Cl & O \\ Cl & O \end{array}$$
 12.58

$$Cl \longrightarrow O NH-N(CH_3)_2$$
 12.60

$$\bigcup_{O} C \subset \bigcup_{NH-N(CH_3)_2}^{O} 12.29$$

$$O_2N - C < O_{NH-N(CH_3)_2} (HL)$$
 11.7

The comparison of the obtained values shows that hydrazide of 4-nitrobenzoic acid has the lowest pK_a

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value and is therefore expected to form most readily the complexes with deprotonated imido form of a ligand.

Indeed, the reactions of Cu and Ni acetates with the given hydrazide in water–alcohol solutions yield, respectively, red and yellow complexes, whose analysis indicates the formation of neutral ML_2 complexes (Table 1).

In IR spectra of ML₂, the bands due to the stretching vibrations v(NH) and v(C=O) typical of a free ligand are lacking, but the bands from the v(C=O) and v(C=N) vibrations appear at 1340 and 1560 cm⁻¹, respectively, which suggests the formation of complexes with the deprotonated imido form of the ligand (Fig. 1b).

The nickel complex NiL₂ is diamagnetic, which confirms its square-planar structure. The diffuse reflection spectrum of this complex contains one band at 455 nm, while that of CuL₂ has two resolved bands at 450 and 550 nm, which is typical of the square-planar Cu(II) complexes. Both complexes are poorly soluble in water, alcohols, and in the most of organic solvents.

In the case of Cu, the imido complexes are formed even in the acidic solutions, when the salts of the strong acids (sulfates, chlorides, etc.) are used in the synthesis:

$$CuSO_4 + 2HL = CuL_2 + H_2SO_4.$$

This makes it possible to conclude that the metal ions shift the equilibrium toward the formation of the imido form. This occurs due to the fact that the neutral ML₂ complexes, particularly those of copper and nickel, have significantly higher stability constants, as compared to the $M(HL)_2X_2$ complexes (where X is an anion of monobasic acid). However, in the case of another metals, such as Mn, Co, Zn, no imido complexes were produced by monitoring pH of the solutions, since their synthesis was complicated by the hydrolysis of the metal salts, whereas in the case with Co, the oxidation of Co^{2+} to Co^{3+} was also observed with the typical electronic absorption spectrum. Therefore, these metals gave only complexes with neutral hydrazide molecules. The results of the chemical analysis of the synthesized complexes are presented in Table 1.

Table 2 contains the main vibration frequencies for the metal hydrazide complexes of amide type that allow one to determine the coordination mode for the hydrazide ligands [7–9]. IR spectra of the complexes contain the absorption band due to the stretching vibrations v(C=O) at 1630–1650 cm⁻¹ (amide I band), the absorption bands from the stretching vibrations v(NH) in the region of 3200 cm⁻¹, and an intense band typical of hydrazides of acids (amide II band) in the range of 1530–1540 cm⁻¹, which is a combined stretchingdeformation vibrations v(C–N). In addition, in this spectrum, one can identify the bands that correspond to the nitro group vibrations: $v_{as}(NO_2)$ at 1520 cm⁻¹ and $v_s(NO_2)$ at ~1350 cm⁻¹.

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Fig. 1. IR spectra of (*a*) *N*,*N*-dimethylhydrazide of 4nitrobenzoic acid (HL), (*b*) CuL_2 , and (*c*) $\text{Ni}(\text{HL})_2(\text{BF}_4)_2$ complexes.

The diffuse reflection spectra of the Co complexes contain one band in the region of 550 nm, while those of the Ni acetate complex with a neutral form of the ligand exhibit the resolved bands due to the ${}^{3}A_{2g} \longrightarrow {}^{3}T_{1g}(P)$ transition (near 370 nm) and the ${}^{3}A_{2g} \longrightarrow {}^{3}T_{1g}(F)$ transition (near 640 nm) of the Ni²⁺ cation in the distorted octahedral surrounding.

When the $[Co(HL)_2(H_2O)_2]Cl_2$ complex is dissolved in an alcohol, the solution color changes from pink to violet, while the electronic absorption spectrum of the solution contains the bands due to the octahedral and tetrahedral forms of the complex. In order to establish the changes in the composition and structure of the complex that occur during its dissolution and to determine the composition of the complexes in the solution, we performed spectrophotometric study of the complexation processes in the CoCl₂–HL–isopropanol and NiCl₂–HL–isopropanol systems.

The composition of the complexes was determined by the molar ratio method with the hydrated metal chlorides used as the starting compounds. A series of solutions was prepared with a constant metal concentration and a variable ligand concentration (from zero to a fivefold excess of L with respect to the metal ions).

As a result of dissolution of the starting CoCl₂ in isopropanol, Co(II) has the coordination surrounding in the form of a distorted tetrahedron ($\lambda = 653$ nm). The complex formation proceeds in steps, which is confirmed by the absence of the isosbestic point (Fig. 2a). The oxidation state of Co remains unchanged during complex formation. It was found that the addition of the first hydrazide molecule to the Co²⁺ ion in a solution gives the tetrahedral complex [Co(HL)Cl₂]. When the

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Fig. 2. The electronic absorption spectra of solutions containing (a) $\text{CoCl}_2(c_{\text{M}} = 0.01 \text{ mol/l})$ and HL ($c_{\text{HL}} = (I) 0, (2) 0.01, (3) 0.015, (4) 0.02, (5) 0.05 \text{ mol/l}$; (b) NiCl₂ ($c_{\text{M}} = 0.01 \text{ mol/l})$ and HL ($c_{\text{HL}} = (I) 0.005, (2) 0.01, (3) 0.015, (4) 0.02, (5) 0.04 \text{ mol/l})$.

second hydrazide molecule is added, the geometry of the Co surrounding changes to the distorted octahedron ($\lambda = 540$ nm), which can be explained by the formation of the $[Co(HL)_2(H_2O)_2]^{2+}$ complex.

One can see from Fig. 3a that even with a fivefold ligand excess, the complex formed in the system has the ratio Co : HL = 1 : 2. The results obtained make it possible to conclude that the change in the electronic absorption spectrum of crystalline Co chloride complex Co(HL)₂Cl₂(H_2O)₂ on dissolution occurs due to its partial dissociation with the formation of tetrahedral complex containing one molecule of hydrazide ligand. The specific behavior of the chloride complex is explained by a sufficiently high coordinating ability of the chloride anion. The dissolution of the Co²⁺ acetate complex does not bring about any noticeable changes in the electronic absorption spectrum.

Since the spectral changes for the NiCl₂-HL-isopropanol system as distinct from the system with Co²⁺,



Fig. 3. The plot of optical density vs. the ratio of the component concentrations in the MCl₂–HL–isopropanol systems at (a) $\lambda_{max} = 654$ nm, M = Co and (b) $\lambda_{max} = 668$ nm, M = Ni.

were insignificant, we recorded the differential absorption spectra of this system (Fig. 2b). For this reason, the spectrophotometric cell was filled not with a solvent but with the initial solution of nickel chloride in isopropanol. The composition of the complexes was found from the relationship between the change in the optical density (ΔD) at $\lambda = 668$ nm and the ratio $c_{\text{HL}} : c_{\text{M}}$. It was shown that, as in the case with Co, only the complexes with the ratio Ni : HL = 1 : 2 are formed in the solution (Fig. 3b), as distinct from the Ni complexes with the unsubstituted hydrazides, which give complexes with three bidentate ligand molecules. This distinctive feature of hydrazide complexes, i.e., the 1,1-dimethylhydrazine derivatives, is explained by the steric effect of two methyl groups at the donor nitrogen atom.

The cyclic voltammogram of HL contains in the anode region the oxidation wave, whose half-wave potential is $E_{1/2} = 0.57$ V. The slope of this wave $\Delta E = E_{3/4} - E_{1/4}$ equal to 110 mV and the lacking wave of

Compound	v(NH)	Amide I, v(C=O)	Amide II, v(C–N)	v(NN), v(HNN)	$\nu(MO), \nu(MN)$	Anion band
HL	3200	1655	1530	1168		
$[Mn(HL)_2(H_2O)_2]Ac_2$	3200	1637	1545	1190	475, 550	1580 (Ac ⁻)
						1410
[Ni(HL) ₂ (H ₂ O) ₂]Ac ₂	3190	1630	1545	1195	480, 555	1590 (Ac ⁻)
						1410
$[Ni(HL)_2(H_2O)_2](BF_4)_2$	3190	1628	1540	1190	480, 560	$1080 (BF_4^-)$
$[Ni(HL)_2(H_2O)_2]Cl_2$	3190	1632	1540	1200	475, 565	
$[\text{Co}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Ac}_2$	3190	1635	1540	1190	475, 570	1595 (Ac ⁻)
						1415
$[Co(HL)_2(H_2O)_2]Cl_2$	3185	1640	1530	1190	475, 560	
$[Zn(HL)_2(H_2O)_2]Ac_2$	3195	1645	1528	1192	470, 555	1580 (Ac ⁻)
						1410

Table 2. Selected vibration frequencies (cm^{-1}) in IR spectra of the synthesized metal complexes with *N*,*N*-dimethylhydrazide of 4-nitrobenzoic acid

reduction at the reverse potential sweep suggest that this oxidation is the electrochemically irreversible process followed by the chemical stage of decomposition of the oxidation product. Since this wave is also observed for the other investigated hydrazides, it can be assigned to the oxidation of the $-NH-N(CH_3)_2$ group. During complexation, this oxidation wave shifts to the anode region, while in the case of the Ni and Co salts, this wave is not observed in the potential region under study. This can indicate the structural changes in hydrazide, in particular, the transformation of the ligand to the imido form, which contains no groups that can be oxidized.

The cathode region of voltammograms of these compounds contains the waves due to the reduction of the NO₂ group with the slope of ≈ 60 mV, which points to the reversible nature of electrochemical process. The waves are readily reproduced with a repeated cycling, i.e., the reduction products are sufficiently stable (in the time scale of voltammometry at the sweep potential rate 10–50 mV/s). In the presence of the Zn²⁺ and Ni²⁺ ions, the reduction waves disappear from the potential region under study, which may be explained by redistribution of the electron density in the hydrazide molecule during complexation and hence, by an increase in hydrazide stability toward the reduction processes.

Thus, *N*,*N*-dimethylhydrazide of 4-nitrobenzoic acid containing the organic radical with a negative induction effect was used to synthesize the Ni and Co

complexes with the deprotonated form of a ligand. Unlike complexes with a neutral form of a ligand, the synthesized complexes are stable with respect to water and common organic solvents and have the higher redox stability.

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