Synthesis and ESR study of Co and Ni hydrazides and hydroxamates containing 2,6-di-*tert*-butylphenol moiety in the ligands

I. A. Zav'yalov,[a] *O. V. Polyakova,*[a] *E. R. Milaeva,*[a]* *and A. I. Prokof'ev*[b]

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8846
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

A series of Co and Ni hydrazides and hydroxamates containing the 2,6-di-*tert*-butylphenol moiety as a potential free radical precursor in the ligand environment of the complexes were synthesized. ESR spectroscopy was used to study the dependence of the stability of metal complexes incorporating a paramagnetic center in the ligand on the type of the coordination environment of the metal and the nature of the ligand. The complexes, in which a saturated aliphatic bridging group separates the 2,6-di-*tert*-butylphenol moiety and the coordination environment of the metal, can undergo oxidation to produce stable paramagnetic species with an unpaired electron in the ligand environment. The interaction of the free radical center in the ligand with the coordination environment of the metal is practically absent (excepting the weak spin-spin interaction). Metal complexes incorporating a hydrazine moiety conjugated with the 2,6-di-*tert*-butylphenol substituent do not produce detectable stable paramagnetic forms with a free radical in the ligand.

Key words: hydrazides, hydroxamates, metal complexes; paramagnetic ligands, ESR spectroscopy.

Natural redox transformations involving metal-containing enzymes and industrial catalytic processes frequently proceed *via* intermediate catalyst forms containing an unpaired electron in the organic ligand environment of the metal complex. The effect of the paramagnetism of a molecule on its reactivity and kinetic and thermodynamic stability is determined by the type of interaction of the unpaired electron of the ligand with the metal atom. Therefore, a problem appears of obtaining model compounds whose ligand environments contain a moiety capable of forming stable paramagnetic species during the redox process. In this case, a possibility appears of a direct ESR study of the interaction between an unpaired electron and the coordination environment of the central metal ion. Sterically hindered phenols that form stable phenoxyl radicals during selective oxidation can be used as such organic groups.[1]

In the present work we obtained, for the first time, hydrazides and hydroxamates of Co^{2+} and Ni^{2+} with the 2,6-di-*tert*-butylphenyl substituent in the ligand environment. The different type of coordination of the metal ions with the ligands and the presence (or absence) of a conjugation chain between the phenoxyl fragment, which is generated due to oxidation, with the coordination centers of these compounds makes it possible to reveal the effect of the chelate structure on the stability of paramagnetic products.

The complexes were obtained from 3,5-di-*tert*-butyl-4-hydroxybenzoyl hydrazide (**1**), 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propionyl hydrazide[2] (**2**), and 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propiohydroxamic acid (**3**).

The complexes were synthesized by reactions of ligands **1**—**3** with the corresponding metal salts in ethanol with heating. The complexation constants of the hydrazides of carboxylic acids and hydroxamic acids with metal (Co, Ni) ions are rather high,[3] which predetermined the high yields of the corresponding metal hydrazides and hydroxamates (**4**—**9**).

The resulting complexes were characterized by elementary analyses, IR spectra, electron absorption spectra, and magnetic moments. Due to formation of the complex compounds, the IR spectra of 3,5-di-*tert*-butyl-4-hydroxybenzoyl hydrazides of Co^{2+} and Ni^{2+} (**4**, **5**) and 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propionyl hydrazides of Co^{2+} and Ni^{2+} (**6**, **7**) display long-wave shift of the absorption bands corresponding to the stretching vibrations of carbonyl groups (by 25 and 35 cm^{-1} for complexes **4**, **5** and **6**, **7**, respectively), bending vibrations of NH_2 groups (by 25 and 20 cm^{-1} for complexes **4**, **5** and **6**, **7**, respectively), and stretching vibrations of NH and NH_2 groups (by 120 cm^{-1} for all compounds) relative to the spectra of the starting ligands. This confirms that the metal ions are coordinated to the

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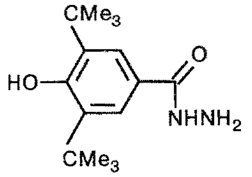
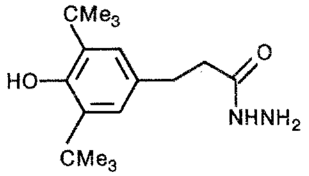


1



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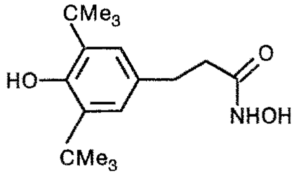

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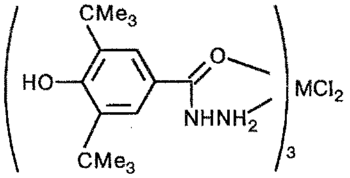
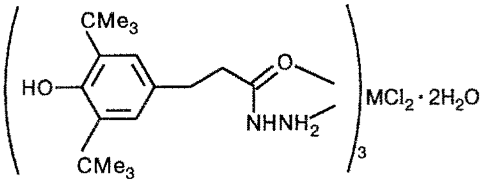
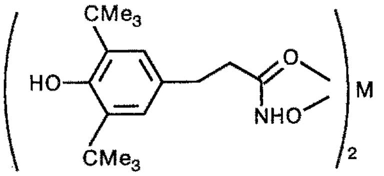


4, 5



6, 7



8, 9

4, 6, 8: M = Co

5, 7, 9: M = Ni

carbonyl groups and the primary amino groups of hydrazides[4] (Table 1).

The electronic absorption spectra of compounds **4**—**7** contain three maxima in the region of 400—700 nm. These maxima are typical of Co^{2+} and Ni^{2+} ions in the octahedral coordination[5] (see Table 1). As a rule, the intensity of the long-wave maximum is small, since the band is masked by absorption corresponding to the ligand—metal charge transfer.

Table 1. Physicochemical characteristics of compounds **1**—**9**

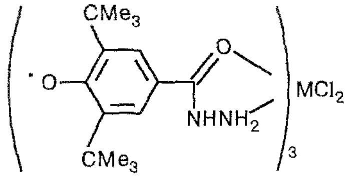
Compound	ν/cm^{-1} (CH_2Cl_2)			λ_{max}/nm (DMF)	μ_{eff}/μ_B (DMF)
	OH	C=O	NH, NH_2		
1	3650	1670	1635, 3340, 3470		
2	3640	1685	1630, 3345, 3450		
3	3635	1660	3400, 3230		
4	3650	1645	1610, 3200, 3410	469.0, 606.4, 672.6	4.78
5	3650	1645	1610, 3200, 3410	460.0, 601.2, 658.3	3.28
6	3648	1650	1610, 3220, 3440	512.0, 606.4, 672.6	4.83
7	3650	1650	1610, 3200, 3440	500.0, 615.3, 665.0	3.32
8	3640	1650	3380	505.0, 612.8, 690.0	4.66
9	3640	1650	3380	495.3, 608.2, 688.3	3.26

The octahedral complexes of divalent cobalt **5** and **7** correspond to the high-spin type ($t_{2g}{}^5e_g{}^2$), and their magnetic moments depend on temperature. The effective magnetic moments of complexes **5** and **7** are smaller than those typical of an ideal octahedral coordination (5.2 μ_B), which indicates that the structure of the complexes slightly differs from an octahedron. The magnetic moments of complexes **6** and **8** are typical of octahedral coordination and do not depend on temperature because their symmetry differs only slightly from an octahedral one.[6]

The structures of hydroxamates **8** and **9** are analogous to metal acetylacetonates.[7] The IR spectra of these compounds do not contain absorption bands corresponding to the stretching vibrations of the hydroxyl group of the starting acid **3**, while the bands corresponding to the stretching vibrations of carbonyl and NH groups are shifted to the long-wave region by 10 and 20 cm^{-1}, respectively. The effective magnetic moment of the high-spin octahedral complex **8** is lower than those of complexes **4** and **6**, which suggests significant distortions of the octahedron. The magnetic moment of octahedral complex **9** does not depend on the distortion of the coordination polyhedron and coincides with the magnetic moments of complexes **6** and **8** (see Table 1).

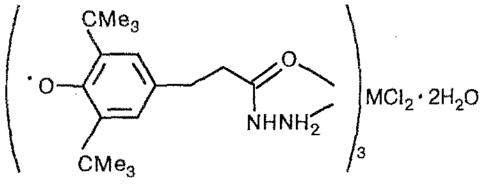
Selective oxidation of compounds **4—9** results in the corresponding phenoxyl radicals **4a—9a**. The paramagnetic metal complexes studied can be divided into two groups, depending on the mutual arrangement of the radical moiety and the coordination metal center in the molecules:

1) radicals **4a** and **5a**, in which the phenoxyl moiety is directly linked to the coordination metal center;

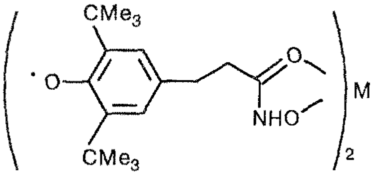


4a, 5a

2) radicals **6a—9a**, whose particular feature is that the phenoxyl moiety is separated from the coordinating moiety by a saturated aliphatic chain.



6a, 7a



8a, 9a

When compound **1** and complexes **4**, **5** were oxidated in solutions, the ESR spectra displayed a broad singlet, which almost instantaneously lost its intensity. A similar spectral picture was obtained for radical forms **6a—9a**. The hyperfine structure of the spectra consists of nine lines (a triplet of triplets) and is determined by the interaction of the spin of an unpaired electron with two protons in the *meta* positions of the phenoxyl ring and two protons of the methylene group. The spectral parameters of complexes **6a—9a** are close to those found for the corresponding radical forms of the starting ligands (Table 2), while the *g*-factors confirm the organic nature of the radicals. The hyperfine coupling constants of the protons in the *meta* positions coincide with similar values typical of 2,6-di-*tert*-butylphenoxyl radicals with alkyl substituents in the *para* position of the aromatic ring.[8] This fact also confirms the absence of considerable interaction between the unpaired electron of the ligand and the metal ions. The slight shift of the *g*-factor for complexes **6a—9a** (in comparison with the spectra of the starting ligands) suggests the presence of only weak spin-spin interaction due to the presence of a metal ion.

Table 2. Parameters of ESR spectra of radicals **2a**, **3a**, and **6a—8a**

Compound	*g*-Factor	*a*(2 H)/G	*a*′(2 H)/G
2a	2.0046	1.60	7.75
3a	2.0045	1.60	8.10
6a	2.0054	1.61	7.75
7a	2.0056	1.60	7.76
8a	2.0057	1.61	8.10

Thus, paramagnetic compounds of the first group, which contain a ligand—metal conjugation system, are characterized by fast decomposition with formation of secondary diamagnetic products, whereas second group radicals are rather stable due to the absence of interaction between the radical fragment and the metal.

Experimental

IR spectra were recorded on a UR-40 spectrophotometer in Vaseline oil and in CH_2Cl_2 and $CHCl_3$ solutions. ^1H NMR spectra were obtained on a Tesla BS-497 spectrometer (60 MHz). The chemical shifts were measured relative to HMDS as the internal standard. $CDCl_3$ and $(CD_3)_2CO$ were used as solvents. UV spectra were recorded on a Varian DMS-100s spectrophotometer in CH_2Cl_2 and DMF. ESR spectra were recorded on a Varian E-12A spectrometer in evacuated tubes at 293 K and 77 K. Toluene, DMF, and pyridine were used as solvents, and PbO_2 served as the oxidant.

3,5-Di-*tert*-butyl-4-hydroxybenzoyl hydrazide (1). A mixture of ethyl 3,5-di-*tert*-butyl-4-hydroxybenzoate (2.1 g, 8 mmol) and hydrazine hydrate (10 mL) was refluxed for 6 h. When the reaction ceased, the solution was cooled, and water (20 mL) was added. The white amorphous compound that precipitated was separated, washed with water, and dried in air. The yield was 87 %, m.p. 181—182 °C (from heptane) (Ref. 9: m.p. 182 °C).

3-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)propionyl hydrazide (2) was obtained from the ethyl ester of the corresponding acid in isopentanol, yield 91 %, m.p. 155—156 °C (from ethanol) (Ref. 2: m.p. 157—158 °C).

3-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)propiohydroxamic acid (3). A solution of KOH (2.7 g, 0.05 mol) in methanol (7 mL) was added at 30—40 °C to a solution of hydroxylammonium hydrochloride (2.1 g, 0.03 mol) in methanol (10 mL). The reaction mixture was cooled and kept for 1 h in a refrigerator, then ethyl 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propionate (4.3 g, 0.015 mol) was added. The mixture was filtered, and the precipitate was washed with methanol (10 mL). The filtrate was kept for 48 h in a refrigerator. The

Table 3. Elementary analysis data, yields, and melting points for compounds **4—9**

Compound	Yield (%)	M.p. /°C	Found/Calculated (%)				Molecular formula
			C	H	N	Cl	
4	65	191—192 (decomp.)	58.63 58.57	8.01 7.81	9.00 9.11	7.51 7.70	$C_{45}H_{72}Cl_2CoN_6O_6$
5	61	188—189 (decomp.)	58.68 58.60	8.05 7.81	8.97 9.12	7.65 7.70	$C_{45}H_{72}Cl_2N_6NiO_6$
6	68	200—201 (decomp.)	58.52 58.73	8.61 8.45	7.85 8.06	6.55 6.81	$C_{51}H_{88}Cl_2CoN_6O_8$
7	62	198—199 (decomp.)	58.68 58.76	8.59 8.45	7.85 8.07	6.62 6.82	$C_{51}H_{88}Cl_2N_6NiO_8$
8	78	162—163	63.28 63.45	8.01 8.09	4.15 4.35		$C_{34}H_{52}CoN_2O_6$
9	70	164—165	63.35 63.48	8.12 8.09	4.22 4.36		$C_{34}H_{52}N_2NiO_6$

crystals that precipitated were filtered off, washed with ethanol, and dried in air. The yield was 57 %, m.p. 142—143 °C (from hexane). Found (%): C, 69.42; H, 9.03; N, 4.82. $C_{17}H_{27}NO_3$. Calculated (%): C, 69.62; H, 9.22; N, 4.78.

Synthesis of complexes 4—9 (general procedure). A salt of a required metal (0.17 mmol) was gradually added with stirring to a hot solution of a ligand (0.4 mmol) in ethanol or methanol. The solution was then heated to boiling and cooled. Water was added to the cooled solution, and the resulting fine-crystalline precipitate was filtered off, washed with water, and recrystallized from an ethanol—water mixture (1 : 1). The yields, melting points, and elementary analysis data are presented in Table 3.

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