

Cobalt(II) Complexes reversibly Uptaking Nitric Oxide in Aqueous Solution

B. JEŻOWSKA-TRZEBIATOWSKA, K. GEREGA, A. VOGT
Institute of Chemistry, University of Wrocław, Wrocław, Poland
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The nitrogen monoxide uptaking by the cobalt complexes with imidazole (Himid) and aminoacids (amac) has been examined. The spectroscopic and stoichiometric results indicate the presence of the $\text{Co(III)(Himid)(amac)}_2\text{NO}$ monomer.

The reversibility of the nitrogen monoxide uptaking by the examined systems has been proved. The existence of the Co(III)NO^- group has been proposed.

Introduction

Co(II) complexes with mixed ligand systems imitating a histidine environment, *i.e.* with imidazole (Himid) and aminoacids (amac), are excellent inorganic oxygen carriers [1–4]. The oxygen molecule reversibly bound to the cobalt complex leads to the formation of a dimer with peroxo-bridge and two Co(III) ions in a molecule [2–4]. Nitric oxide contains one electron less in the molecule than the oxygen O_2 and it was interesting to study the NO uptaking by the known established oxygen carriers.

A number of nitrosyl cobalt complexes is already known [6–11] but the reverse NO uptaking has been found in few complexes only [12].

This paper is the report of the results for Co(II) complexes with aminoacids and imidazole reversibly binding gas NO molecules.

Experimental

In synthesis of samples of both forms (active and NO containing one) the Co(imid)_2 complex prepared as given in [1] was employed.

The solution samples of the active form were synthesised and stored under oxygen-free atmosphere to avoid the formation of the oxygenated forms, *i.e.* the dimer complexes containing the μ -peroxo bridge [3, 4, 13, 14].

The NO containing form was synthesised and stored under nitrogen monoxide atmosphere at 0 °C. At 0 °C and 1 atm the saturation of a system was almost complete.

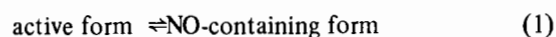
The spectroscopic measurements in VIS were made on a Cary 14 spectrophotometer in a thermostated cell at 0–0.1 °C, using cuvettes of $d = 0.1$ and 0.5 cm. The cuvettes were filled up with a solution of active form in glass apparatus (our construction).

The cuvettes were filled up with the NO containing form in a thermostated room at 0 °C, in dry-box filled with NO diluted in argon. Total concentration of cobalt was equal to 3.6×10^{-2} – 3.7×10^{-2} M.

Volumetric measurements were made at 0 °C, in an isobaric measurement system. The following cobalt nitrosyl complexes with imidazole and the following α -aminoacids: glycine, L-alanine, L-glutamine, L-citrulline, L-arginine, L-ornithine, L-lysine, L-threonine and L-proline were examined.

Results and Discussion

The reversible nitrogen monoxide fixation by the system Co–imidazole–aminoacid, could follow in many cycles:



without remarkable lost of efficiency of the system. Spectroscopic measurements revealed the only insignificant change of the bands extinction in the spectrum of NO containing complex after subsequent gas uptaking and detachment cycles. However, the NO containing form undergoes slow intramolecular oxidation, upon storage peculiarly at increased temperature and in repeated subsequent gas uptaking cycles by the system (like the oxygenated systems).

The shift of equilibrium can be achieved by the change of temperature or of the partial NO pressure over the solution. The complete shift of equilibrium towards the active form is observed either at 50–60 °K ($P_{\text{NO}} = 1$ atm) or at any temperature under neutral gas atmosphere.

The temperature increase accelerates the NO detachment process more than the passing of the neutral gas through the solution. Almost maximal saturation of the NO system can be achieved at an NO pressure equal to 1 atm at 0 °C (see below).

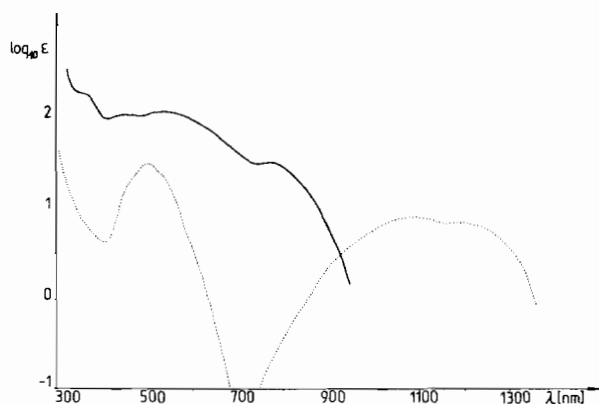


Figure 1. Absorption spectra of a) Co(II)(Himid)(amac)₂NO; b) Co(II)(Himid)(amac)₂H₂O (.....).

To establish the stoichiometric composition of the system the volumetric determination of the nitrogen monoxide, up-taken by the active form at 0 °C as well as determination of imidazole liberated in the synthesis of the NO-containing form were made. From the spectroscopic data it was possible to estimate the shift of equilibrium (1) towards the NO containing form at 0 °C and at $P_{\text{NO}} = 1$ atm. Under such conditions there exists in solution only the form with bound NO (lack of the band at about 1100 nm characteristic of active form). It allowed to interpret the volumetric measurements data.

The measurements made for all the systems with various aminoacids indicated the formation of the

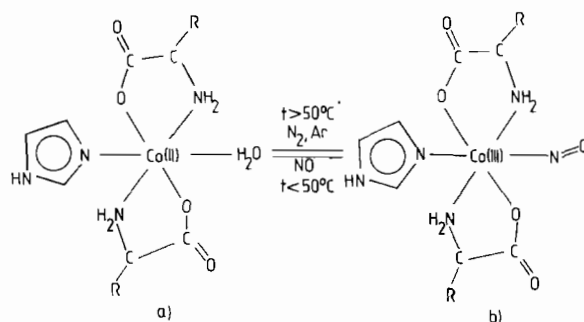


Figure 2. Proposed structure of a) "active" and b) NO containing forms of the complexes.

monomeric complexes with the uptaken nitrogen monoxide (Co:NO = 1:1). Knowing the stoichiometry of NO-containing complex, it was possible to establish precisely the shift of equilibrium (1) towards the form containing the bound gas molecule, which is equal at least to 80%, depending on the aminoacid ligand.

We established the liberation of imidazole in the synthesis of both forms of complexes, which is the reason of pH increase of the reacting solution up to 8–9 in relation to the pH of aminoacid solution. We have made the quantitative determination of liberated imidazole by potentiometric titration of that compound in the filtrate after isolation of NO containing form from the solution with acetone, at 0 °C.

The isolated imidazole was potentiometrically titrated by 1N H₂SO₄.

TABLE I. Spectral Properties.

Complex	ν_1 ${}^1T_{2g} \leftarrow {}^1A_{1g}$		ν_2 ${}^1T_{1g} \leftarrow {}^1A_{1g}$		ν_3 ${}^3T_{1g} \leftarrow {}^1A_{1g}$	
	cm ⁻¹	(ϵ)	cm ⁻¹	(ϵ)	cm ⁻¹	(ϵ)
Co(Himid)(citrulline) ₂ NO	29400	(211)	22200 19050	(109) (114)	13200	(32)
Co(Himid)(L-threonine) ₂ NO	28400	(191)	22200 19000	(113) (116)	13500	(33)
Co(Himid)(glycine) ₂ NO	28400	(174)	21950 19000	(99) (101)	13500	(30)
Co(Himid)(ornithine) ₂ NO	28400	(197)	22450 19000	(110) (112)	13300	(32)
Co(Himid)(alanine) ₂ NO	28400	(221)	22200 19000	(122) (120)	13200	(31)
Co(Himid)(glutamine) ₂ NO	28400	(203)	21950 19000	(113) (116)	13200	(31)
Co(Himid)(arginine) ₂ NO	28400	(199)	22200 19000	(116) (121)	13300	(34)
Co(Himid)(proline) ₂ NO	29400	(254)	22450 19000	(126) (132)	13200	(36)
Co(Himid)(lysine) ₂ NO	28400	(205)	22200 18800	(117) (117)	13400	(35)

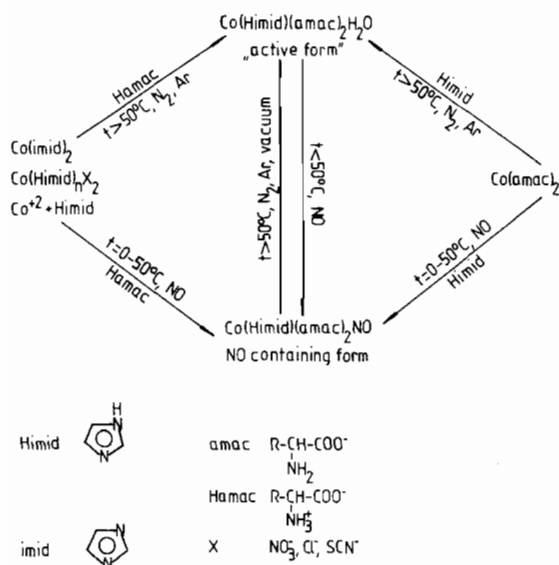


Figure 3. Scheme of synthesis reaction of the active and NO containing form of complexes.

The results of those determinations indicate the liberation of one imidazole molecule per one cobalt atom.

Hence, there are one NO and one imidazole molecule in the NO-containing complex. The other coordination sites are occupied by two aminoacid molecules, which coordinate through NH_2 and COO^- groups at pH 8–9 (Fig. 2).

As active complex form the NO molecule is replaced by H_2O . The oxidation state and electronic structure of cobalt in both forms of the system were proposed on the basis of the spectroscopic studies in solution and the magnetic investigation.

In the VIS and IR region (Fig. 1) of active form species two bands are present – at about 1100 nm ($\epsilon \sim 10$) and at about 500 nm ($\epsilon \sim 30$) with two shoulders at about 530 nm and 460 nm, respectively.

The spectra are characteristic for high-spin Co(II) six-coordinate complexes. The absorption spectra obtained at 0°C (1 atm of NO) of a complex with band NO molecule could be assigned as for six-coordinate low-spin Co(III) ion in tetragonal environment [6, 11]

The transition energy 715–755 nm is spin forbidden $^1A_{1g} \rightarrow ^3T_{1g}$. The other two bands at about 460 and 530 nm belonging to $^1A_{1g} \rightarrow ^1T_{1g}$ transition are split by distortion of the O_h symmetry. The highest energy band at 340–350 nm could be assigned to $^1A_{1g} \rightarrow ^1T_{2g}$ transition.

Comparison of the transition energies for complexes with different aminoacids (Table I) revealed

insignificant dependence on the coordinated aminoacid. Thus the influence of side-chain groups on the formed complex could be negligible at least in spectroscopic studies. Magnetic investigations indicated the diamagnetism of the form with the uptaken NO. Hence the active form of system which is high-spin six-coordinate Co(II) complex transforms into the low-spin six-coordinate Co(III) complex by replacement of H_2O molecule by NO. This is combined with the electron transfer from the upper occupied cobalt orbital to the higher half-occupied acceptor molecular orbital of nitrogen monoxide.

The reverse process is observed with NO liberation from the system with changing NO pressure over the solution or with changing temperature (Fig. 3).

The diamagnetism of complexes with the uptaken nitrogen monoxide could be explained by assuming a non-linear coordination of the gas molecule. This makes possible the electron transfer from the donor high-spin d_{z^2} orbital of cobalt(II) ion to the π -antibonding orbitals via the σ bonding. Those orbitals degenerated in the free molecule undergo splitting due to the non-linear coordination. The splitting is large enough so that the electron transfer from the metal ion occurs to the lower π -antibonding orbital. This results in the spin pairing on one π -antibonding orbital. The newly formed $\sigma(d_{z^2} + \pi^*)$ molecular orbital has mainly ligand NO character.

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