



Polymeric and mixed ligand complex of cobalt(II) and 4-hydroxybenzhydrazide: Crystal structure and vibrational spectroscopy

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ARTICLE INFO

Article history:

Received 20 April 2010

Received in revised form 21 June 2010

Accepted 21 June 2010

Available online 8 July 2010

Keywords:

4-hydroxybenzhydrazide

Deuteration

DFT calculations

Normal modes

ABSTRACT

Reaction of CoSO_4 and 4-hydroxybenzhydrazide in water/methanol solution resulted in polymeric complex with C=O and NH_2 groups of organic ligand, two water molecules and two oxygen atoms of two sulfate anions in metal coordination sphere. The X-ray analysis revealed that the complex is in the form of polymer chain of the helical structure formed due to sulfate bridge geometry and intra-chain hydrogen bonds. The variety of coordinated ligands is reflected in the vibrational spectra where six different metal–ligand modes were found. The bands related to stretching and bending vibrations of NH_2 , NH , OH groups as well as water molecules were located with help of hydrogen–deuterium substitution. For proposed band assignment the animation of DFT calculated normal modes was employed.

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1. Introduction

A considerable number of coordination compounds is formed with the elements belonging to the VIII-th group of the periodic table. In the set of ferrous metals, the chemistry of the cobalt complexes is particularly advanced and reflects the cobalt ion capability of binding a wide range of organic as well as inorganic ligands, including solvent molecules. The metal itself is relatively uncommon but its compounds have been in use for centuries, mostly as pigments (cobalt blue) in glass and porcelain. The properties of that element are notable for the ease with which complexes are formed and complex formation stabilizes the +2 and +3 metal oxidation states. Usually, the vicinity of cobalt in coordination compounds is characterized by the octahedral, rarely by the tetrahedral geometry, where that former has been found in cobalamin (vitamin B12). The vitamin B12 consists of central Co atom, which occurs in the unusual range of +1 to +3 oxidation stage, flat spacious corrine ring in the equatorial and two ligands in the parallel positions. One of the coordination bonds is the type of Co–C, what makes the cobalamin the only known naturally occurring metalloorganic compound [1].

The diversity of molecules, which can bind the cobalt ion and form new compounds of interesting properties, allowed us to concern the 4-hydroxybenzhydrazide (4hbah) as a ligand in reactions with cobalt salts. As described in previous articles [2,3], 4hbah belongs to a class of hydrazine derivatives, well known for different biological, analytical and agricultural applications. The most famous hydrazide is the isonicotinic acid hydrazide (isoniazide, anti-

tuberculosis drug) and it is different from 4hbah only by the presence of pyridine ring instead of 4-hydroxybenzene group. However, 4hbah shows moderate antimicrobial activity [4], it has been found that it increases the resistance against the tomato wilt disease [5] and can be attractive subject of further chemical and biological investigations.

In the literature a few examples of 4hbah complexes with transition metals have been reported. The research has been mainly focused on the copper(II) [6–14] and nickel(II) [6,7,11,14] complexes. Only two communications have taken into account the 4hbah complexes with dithionate cobalt salts [7,14]. Based on the infrared spectroscopic measurements, the authors have proposed the general formula of the complexes $(\text{MeL}_n\text{S}_2\text{O}_6 \cdot m\text{H}_2\text{O})$ where $n = 2, 3$; $m = 0, 1, 2$; L – various benzhydrazides) and coordination mode through the N-amino and O-carbonyl atoms without any deeper consideration of the cobalt coordination environment, which frequently is completed by the solvent molecules.

Herein was described the preparation and crystal structure of a new 4hbah complex with cobalt(II) sulfate(VI) where the 4-hydroxybenzhydrazide, SO_4 groups and solvent molecules are involved in metal binding. Additionally, the detailed analysis of vibrational spectra was performed, enhanced by the O,N-deuteration and DFT calculations.

2. Experimental

2.1. Synthesis and physical measurements

The $[\text{Co}(\text{H}_2\text{O})_2(4\text{hbah})(\mu\text{-SO}_4)]_n$ complex was synthesized in the reaction of 0.1 mmol commercially available 4-hydroxybenzhydrazide

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(Aldrich) in 5 cm³ warm CH₃OH/H₂O (3:2) solution with 0.1 mmol cobalt(II) sulfate(VI) (Aldrich) in 3 cm³ water solution. After 1 day incubation in room temperature the pink crystals suitable for X-ray investigation were obtained. Calculated for C₇H₁₂N₂O₈ScO (%) : C, 24.50; H, 3.52; N, 8.16; S, 9.34. Found: C, 24.60; H, 3.38; N, 8.09; S, 9.27.

The preparation of O,N-deuterated isotopologue was preceded by twofold recrystallization of 4-hydroxybenzhydrazide from CH₃OD/D₂O solution and further carried out as for natural complex. The deuteration efficiency of more than 90% was estimated from the ratio of the integrated intensities of the absorption at 1648 cm⁻¹.

The IR spectra have been measured on Perkin–Elmer FT-IR 2000 spectrometer with 2 cm⁻¹ resolution, applying 64 scans and KBr pellet technique for middle-IR and 300 scans and sample immersed in Nujol mull for far-IR region.

Raman spectrum has been recorded on Horiba Jobin Yvon HR800 dispersive Raman spectrometer equipped with a microscope, laser diode (785 nm), operating in Sol–Gel Nanotechnology Materials Laboratory of Lower Silesian Centre for Advanced Technologies in Wrocław. Final spectrum was computed with 1.5 cm⁻¹ resolution from 16 scans measured at the back-scattering geometry.

2.2. X-ray analysis

The [Co(H₂O)₂(4hbah)(μ-SO₄)_n] crystal was measured on a KUMA KM4CCD diffractometer with the Mo Kα radiation (λ = 0.71073 Å) at 100 K with applying Lorentz and polarization corrections. The crystal structure was solved by direct methods option in SHELXS97 program [15] and refined by the full-matrix least-squares method on all F² data using the Sheldrick's SHELXL97 software [16]. The positions of heavy atoms were refined with anisotropic thermal parameters, whereas the hydrogen atoms were located in the difference Fourier syntheses and refined with isotropic thermal parameters. Other additional details and crystal data are included in Table 1. Molecular graphics were prepared using the ORTEP application [17] whereas the selected crystal parameters were calculated employing the PARST97 program [18].

Table 1
Crystal data for [Co(H₂O)₂(4hbah)(μ-SO₄)_n].

Empirical formula	C ₇ H ₁₂ CoN ₂ O ₈ S
Formula weight	343.18
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	
<i>a</i> (Å)	13.419(3)
<i>b</i> (Å)	5.720(2)
<i>c</i> (Å)	15.309(4)
β (°)	103.13(3)
Volume (Å ³)	1144.3(6)
<i>Z</i>	4
<i>D</i> _{calc} (Mg/m ³)	1.992
Absorption coefficient (mm ⁻¹)	1.723
<i>F</i> (0 0 0)	700
Crystal size (mm)	0.15 × 0.13 × 0.11
θ range for data collection (°)	2.73–36.79
Index ranges (limiting indices)	–22 ≤ <i>h</i> ≤ 21, –9 ≤ <i>k</i> ≤ 8, –24 ≤ <i>l</i> ≤ 24
Reflections collected/unique	19110/4842 [R _{int} = 0.0277]
Refinement method	Full-matrix least-squares on F ²
Data [I > 2σ(I)]/parameters	4842/0/172
Goodness-of-fit on F ²	1.060
Final R indices [I > 2σ(I)]	R ₁ = 0.0263, wR ₂ = 0.0683
R indices (all data)	R ₁ = 0.0391, wR ₂ = 0.0732
Largest peak difference and hole (e Å ⁻³)	0.709 and –0.382

2.3. Theoretical DFT calculations

The quantum calculations were performed applying the GAUSS-IAN09 package [19], at DFT level, using the B3LYP functional [20] and LanL2DZ basis set [21]. For the structure optimization followed by computation of normal vibrations, the [Co₂(H₂O)₂(4hbah)(μ-SO₄)₂] molecular fragment the same as shown in Fig. 1 was extracted from complex polymeric chain. The starting structural parameters were taken from the X-ray measurements.

In the optimized structure of the [Co₂(H₂O)₂(4hbah)(μ-SO₄)₂], the quasi-octahedral structure of cobalt(II) coordination sphere and sulfate bridging mode were preserved.

Using the optimized structural parameters, the wavenumbers, IR intensities, Raman activities and atom displacements for all normal vibrations were computed with harmonic approximation. The computed frequencies were not scaled. Molden application was applied for the visual animation of normal vibrations and generation of both theoretical IR and Raman spectra [22].

3. Results and discussion

3.1. Description of the [Co(H₂O)₂(4hbah)(μ-SO₄)_n] structure

The arrangement of the simplest structural unit [Co(H₂O)₂(4hbah)(μ-SO₄)] with adjacent sulfate group belonging to the next unit is shown in Fig. 1. In the metal coordination, the 4hbah acts as a bidentate ligand which employs carbonyl oxygen and a terminal nitrogen atom of the hydrazide, contributing in the five-membered chelate ring. Such coordination mode is typical for hydrazides [23]. The organic ligand, together with two water molecules and two SO₄²⁻ groups occupy six positions of Co(II) coordination polyhedron. Each sulfate group links two neighbor metal atoms causing the formation of an infinite polymeric chain. The *cis* position of sulfate groups bonded to the same Co atom results in helical shape of the whole coordination polymer (Fig. 2).

Selected structural parameters of the metal environment are compiled in Table 2. It was assumed that three oxygen (O1w, O2, O3) and one nitrogen (N2) atoms form the quasi-planar base of the coordination square-bipyramid, meanwhile the apical positions are occupied by the oxygen atoms of water molecule (O2w) and sulfate anion (O4). The position of O2w is almost perpendicular to this basal plane (deviation is 2.08°) whilst the O4 atom is slightly (4.60°) displaced from the normal to that plane towards to O1w and O3 atoms. The shortest CoO bonds are formed between central atom and O1w and O2w oxygen atoms of water molecules with respective distances equal 2.076(1) and 2.057(1) Å. The lengths of bonds involving cobalt(II) and SO₄ oxygen atoms are 2.112(1) and 2.143(1) Å, which are in agreement with the literature data, where the similar CoO bond lengths of 2.105 and 2.153 Å [24,25] are reported.

The distances and angles in the SO₄ group are in accordance with those generally observed in sulfates(VI) [1,24,26]. The participation of O3 and O4 atoms in metal coordination should influence the lengths of S–O3, S–O4 bonds, but surprisingly, only the S–O3 bond is slightly longer than three remaining bonds (Table 2). This untypical behavior could be explained by the O2w–H22...O3 hydrogen bond, which can cause some displacement of the O3 atom and elongation of the Co–O3 bond, in comparison with Co–O4 bond where the oxygen atom does not participate in any H-bonding.

The review of all hydrogen bonds indicates that [Co(H₂O)₂(4hbah)(μ-SO₄)] takes advantage of the HOH, OH, and NH groups as donors and simultaneously the OH and SO₄ groups as acceptors. Lengths and angles of hydrogen bonds are collected and numbered in Table 3. The hydrogen bonds could be classified into two sets:

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