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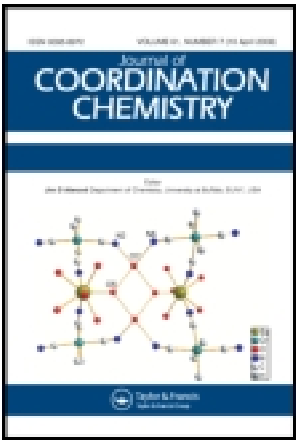

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X-ray structure and vibrational spectroscopy of a cobalt(II) complex prepared with excess of 4-hydroxybenzhydrazide

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A new cobalt(II) complex was obtained from CH_3OH/H_2O solution containing $CoSO_4$ and 4-hydroxybenzhydrazide (4hbah) in 1 : 3 molar ratio. The crystals are composed of polymer chains $[Co(4hbah)_2(\mu\text{-}SO_4)]_n$ accompanied by lattice H_2O and CH_3OH forming the 3-D network. The CH_3OH molecules are highly disordered. For the assignment of IR and Raman spectra, the O,N-deuterated compound was prepared and DFT calculations were carried out.

Keywords: 4-Hydroxybenzhydrazide; Cobalt(II) complex; Complex polymer chain; Deuteration; Normal vibrations

1. Introduction

Hydrazides are organic compounds primarily known for their medical applications in the treatment of tuberculosis [1, 2] as well as antibacterial agents and fungicides [3, 4]. Hydrazides are good ligands for binding metal ions and their coordination chemistry has grown since it was discovered that metal complexes have stronger antimicrobial action than pure ligand and metal salt [3–5]. The last possibility stimulates our efforts in the preparation of new metal complexes with 4-hydroxybenzhydrazide (4hbah), to be further tested for biological activity. However, before biological testing, we intensively investigate the structures and spectroscopic properties of newly obtained compounds, as a contribution to the coordination chemistry of hydrazide complexes.

Another area of our interest is coordination polymers [6–8], which have attracted growing attention. The most promising applications of such compounds are for materials called metal-organic frameworks (MOFs) [9, 10]. In construction of such materials the linkers, organic ligands of appropriate molecular shape and location of coordinating centers, to provide the desired separation between metal ions, are most important. In some cases, the growing coordination polymer in the crystalline state is not caused by main, multi-functional ligand, but by additional molecule acting as linker. Among possible inorganic linkers, sulfate offers one or two coordination centers [11]. The latter mode we recently found in the Co(II) complex with

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4-hydroxybenzhydrazide (4hbah), where the *cis* location of two cobalt–sulfate bonds resulted in helical structure of the polymer chain [12].

In this article, we report another cobalt(II)–4-hydroxybenzhydrazide polymer of linear structure forced by more symmetric composition of the metal coordination sphere. The X-ray structure is accompanied by the interpretation of IR and Raman spectra, where special attention was paid on the vibrations of metal and sulfate.

2. Experimental

2.1. *Synthesis and physical measurements*

In contrast to previously reported $[Co(H_2O)_2(4hbah)(\mu\text{-}SO_4)]_n$ [12], the precipitation of present compound was forced by excess of the organic ligand in relation to metal salt as well as relatively low content of water in the water–methanol solvent. For complex preparation, 0.2 mmol of commercially available 4-hydroxybenzhydrazide (Aldrich) was dissolved in boiling mixture of 2.5 mL CH_3OH and 0.5 mL H_2O. The evaporated methanol was successively replenished to the starting volume. The warm ligand solution was mixed with warm 1.0 mL water solution containing 0.07 mmol of $CoSO_4$, filtered, and supernatant was kept in a closed vial for 1 day at 40°C. Final product as cube salmon crystals was filtered off, washed with methanol, and dried in air. Anal. Calcd for $C_{15}H_{22}O_{10}N_4SCo$ (%): C, 35.37; H, 4.35; N, 11.00; S, 6.29. Found (%): C, 34.87; H, 4.45; N, 11.03; S, 6.59.

2.2. *X-ray crystallography*

Crystal with approximate dimensions of 0.15 mm × 0.12 mm × 0.11 mm was used for data collection. Data were collected at 100 K using a KM4-CCD diffractometer and graphite-monochromated Mo-Kα radiation generated from a diffraction X-ray tube operated at 50 kV and 20 mA. The images were indexed, integrated, and scaled using the Oxford Diffraction data reduction package [13]. The experimental details together with the crystal data are given in table 1. The structure was solved by direct methods using SHELXS97 [14] and refined by full-matrix least-squares on all F^2 data [15]. Non-H atoms were included in the refinement with anisotropic displacement parameters; hydrogens were included from the geometry of molecule; only H atoms bonded to O and N atoms were found from difference map and constrained. The data were corrected for absorption, min/max absorption coefficients are 0.659 and 0.730. Crystallization methanol molecules are highly disordered and could not be refined adequately. To avoid this problem the SQUEEZE procedure [16] was applied using PLATON [17]. The structure has been deposited with the CCDC. Molecular graphics were prepared using the ORTEP application [18], whereas the selected crystal parameters were calculated employing the PARST97 program [19].

2.3. *Spectral measurements*

The Perkin-Elmer FT-IR 2000 spectrometer has been used for IR spectra collection. The KBr pellet technique has been applied for middle-IR measurements

Table 1. Crystal data and structure refinement for $\{[\mathrm{Co(4hbah)_2(\mu\text{-}SO_4)}]\cdot\mathrm{H_2O}\cdot\mathrm{CH_3OH}\}_n$.

Empirical formula	$C_{14}H_{18}CoN_4O_9S$
Formula weight	476.32
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P*2(1)/*c*
Unit cell dimensions (Å, °)	
a	15.523(4)
b	6.623(3)
c	19.232(5)
β	104.56(4)
Volume (Å^3), *Z*	1913.7(11), 4
Calculated density, D_{Calcd} (Mg m^{-3})	1.657
Absorption coefficient (mm^{-1})	1.063
F(000)	980
Crystal size (mm^3)	0.15 × 0.12 × 0.11
θ range for data collection (°)	2.58–25.07
Index ranges (limiting indices)	$-18 \le h \le 18$; $-7 \le k \le 6$; $-22 \le l \le 22$
Reflections collected/unique	12,852/3387 [$R_{\mathrm{int}} = 0.0463$]
Refinement method	Full-matrix least-squares on F^2
Data [$I > 2\sigma(I)$]/parameters	3387/0/265
Goodness-of-fit on F^2	0.995
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0379$, $wR_2 = 0.0665$
R indices (all data)	$R_1 = 0.0650$, $wR_2 = 0.0946$
Largest peak difference and hole (e Å^{-3})	0.445 and −0.363

(2 cm^{-1} resolution, 64 scans), whereas samples immersed in Nujol mull were used for far-IR region (2 cm^{-1} resolution and 300 scans).

For Raman spectrum acquisition the Horiba Jobin Yvon HR800 dispersive Raman spectrometer, equipped with a microscope and laser diode (785 nm), was used. Final spectrum was computed with 1.5 cm^{-1} resolution from 16 scans measured at the back-scattering geometry.

2.4. *Computational methods*

Quantum-mechanical calculations, enhancing interpretation of vibrational spectra, were performed using the Gaussian09 package [20]. The structure optimization and normal mode calculation were performed employing the B3LYP functional [21] and LanL2DZ basis set [22], expanded with d-polarization functions on carbon and nitrogen. The normal vibrations were visually animated using the Avogadro program [23], whereas the theoretical IR and Raman spectra were generated employing the Molden application [24].

3. Results and discussion

3.1. *Description of the* $\{[\mathrm{Co(4hbah)_2(\mu\text{-}SO_4)}]\cdot\mathrm{H_2O}\cdot\mathrm{CH_3OH}\}_n$ *structure*

$[\mathrm{Co(4hbah)_2(\mu\text{-}SO_4)}]_n$ is a polymer chain composed of cobalt(II), sulfate, and organic molecules as 4-hydroxybenzoic acid hydrazide (4hbah). The smallest distinctive

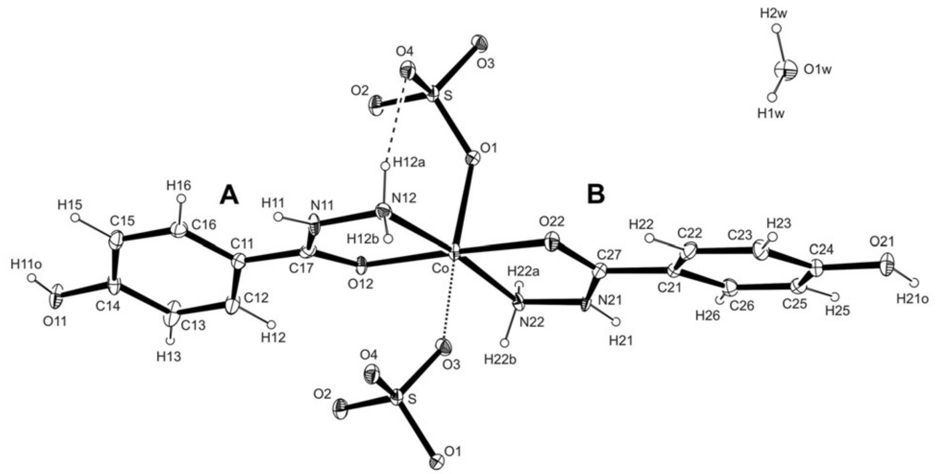

Figure 1. The asymmetric $[Co(4hbah)_2(\mu\text{-}SO_4)] \cdot H_2O$ unit with neighbor sulfate group at equivalent position x, $y-1$, z. Thermal ellipsoids are shown with 50% probability.

structural unit building the polymer and the atom-numbering system are shown in figure 1. Selected bond lengths and angles of the complex are listed in table 2.

The 4hbah is a neutral ligand, coordinating bidentate through terminal nitrogen as well as carbonyl oxygen; 4hbah ligands are *trans*. Most of the skeletal parameters of organic ligands are very similar, with maximum difference in bond lengths of less than 0.002 Å and in plane angles below 2°. Comparative difference was also found in mutual orientation of aromatic and chelate rings. For ligand **A** (figure 1), the best planes of mentioned rings form the dihedral angle of 16.34°, whereas in ligand **B** similar angle is 13.95°. Such difference in both ring orientation is additionally demonstrated by dihedral angles around the C–C bonds, linking the aromatic and chelate rings.

The distances between Co(II) and coordinated atoms are almost equal for oxygen, O12 and O22 (2.064 and 2.055 Å, respectively) and nitrogen, N12 and N22 (2.130 and 2.139 Å, respectively). O12, O22, N12, and N22 do not form an ideal plane, but are displaced from their best plane. The crystallographic data show that the oxygens are above, while the nitrogens are under the plane, with the displacements of about 0.050 Å. This plane can be considered as a basal plane of distorted coordination polyhedron in which the apical position is occupied by O1 of SO_4. The Co–O1 bond of 2.121(2) Å is almost perpendicular to the mentioned best plane forming 4.4(1)° angle with the normal to that plane. Despite the smallest unit exhibiting a five-coordinate cobalt(II), in fact it is octahedral with the sixth coordination place occupied by O3 of sulfate from the next unit, shown in figure 1 by a dashed line. A polymer chain, along the *b*-axis, is formed. The position of O3 is also not perpendicular to the best basal plane and presents similar deviation as is observed for Co–O1, namely in the direction of **B** ligand chelate ring. The Co–O3 distance (2.165 Å) is the longest in the quasi-octahedral metal surrounding, but its length is comparable with finding in the literature data where similar SO–Co bond of 2.153 Å is reported [25]. In contrast to the position of O1 and O3, the opposite effect is observed for the remaining oxygens of sulfate which are slightly shifted toward

Table 2. Selected structural parameters: bond lengths (Å) and angles (°) for $\{[\mathrm{Co(4hbah)_2(\mu\text{-}SO_4)}]\cdot \mathrm{H_2O}\cdot \mathrm{CH_3OH}\}_n$.

Bond lengths (Å)			
Co–O1	2.121(2)	Co–O3$^{\mathrm{i}}$	2.164(2)
Co–O12	2.064(2)	Co–O22	2.055(2)
Co–N12	2.130(3)	Co–N22	2.139(3)
N12–N11	1.420(4)	N22–N21	1.422(3)
N11–C17	1.336(5)	N21–C27	1.336(5)
C17–O12	1.264(4)	C27–O22	1.250(4)
S–O1	1.507(2)	Ow1–H1w	0.819(3)
S–O2	1.456(2)	Ow1–H2w	0.820(2)
S–O3	1.474(2)		
S–O4	1.475(3)		
Bond angles (°)			
Co–N12–N11	107.3(2)	Co–N22–N21	107.3(2)
N12–N11–C17	119.1(3)	N22–N21–C27	117.9(2)
N11–C17–O12	119.7(3)	N21–C27–O22	121.2(3)
C17–O12–Co	115.1(2)	C27–O22–Co	114.9(2)
C17–C11–C12	118.7(3)	C27–C21–C22	117.0(3)
C13–C14–O11	116.9(3)	C23–C24–O21	116.9(3)
O1–Co–O12	93.0(1)	O1–Co–O22	88.4(1)
O1–Co–N12	97.8(1)	O1–Co–N22	89.2(1)
O12–Co–O22	177.8(1)	N22–Co–N12	172.8(1)
O12–Co–N12	78.6(1)	N22–Co–O22	78.6(1)
O12–Co–N22	99.8(1)	O22–Co–N12	102.9(1)
S–O1–Co	132.4(1)	O2–S–O3	111.5(1)
O1–S–O2	109.8(1)	O2–S–O4	110.8(1)
O1–S–O3	106.2(1)	O3–S–O4	109.9(1)
O1–S–O4	108.4(1)	H1w–O1w–H2w	105.6(3)
Dihedral angles (°)			
O12–C17–C11–C12	17.9(5)	O22–C27–C21–C22	15.3(5)
Co–N12–N11–C17	–5.6(3)	Co–N22–N21–C27	–2.2(3)
N12–N11–C17–O12	2.1(4)	N22–N21–C27–O22	–179.5(3)
O1–Co–O3$^{\mathrm{i}}$–S$^{\mathrm{i}}$	–153.5(2)	O3$^{\mathrm{i}}$–Co–O1–S	179.3(2)

Equivalent positions: $^{\mathrm{i}}$: x, $y-1$, z.

A 4hbah ligand. This structural phenomenon is probably caused by the presence of an intramolecular hydrogen bond (table 3 and figure 1) between N12–H12a $\cdots$ O4.

The tetrahedral structure of $\mathrm{SO_4^{2-}}$, considering the S–O bonds and O–S–O angles, is more or less like in other compounds containing sulfate [26, 27]. However, two bonds are slightly different; the S–O1 bond as a coordinating oxygen is a little longer and S–O2 a little shorter. The sulfate is important not only for compensating the positive charge of cobalt cation, but also for elongating the polymer chain, where $\mathrm{SO_4^{2-}}$ is a bridging co-ligand and for intermolecular interactions, especially hydrogen bonds.

The chemical formula shows that the smallest structural unit contains water and methanol crucial for hydrogen bonding. Unfortunately, from the X-ray measurement only the position of water was found; the methanols are disordered. It was necessary to assess the methanol stoichiometry by using elemental analysis, which shows that the molar content of $\mathrm{CH_3OH}$ is close to the content of $\mathrm{H_2O}$ and $[\mathrm{Co(4hbah)_2(\mu\text{-}SO_4)}]$. Nevertheless, further description of the crystal structure will not concern the $\mathrm{CH_3OH}$ molecules.

Applying the structural criteria ($\mathrm{D}\cdots\mathrm{A} \leq 3.2$ Å and $\mathrm{D{-}H}\cdots\mathrm{A}$ angle $\geq 130°$) [28] for strong and moderate hydrogen bonds to the inspection of intermolecular interactions,

Table 3. Numbering and structural parameters of hydrogen bonds in $\{[Co(4hbah)_2(\mu\text{-}SO_4)]\cdot H_2O\cdot CH_3OH\}_n$ (Å, °).

Lp.	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
	Intraunit				
1	N12–H12a···O4	0.86	2.33	3.030(4)	138
	Interunit				
2	O1w–H1w···O12^{ii}	0.82	2.14	2.858(3)	147
3	O1w–H2w···O2^{iii}	0.82	1.96	2.745(4)	160
4	N22–H22b···O1w^{iv}	0.86	2.51	3.149(4)	131
5	N21–H21···O1w^{v}	0.86	1.92	2.759(4)	163
6	O21–H21o···O1^{v}	0.84	1.88	2.695(3)	165
7	O11–H11o···O4^{vi}	0.71	1.99	2.648(3)	153
8	N22–H22a···O21^{iv}	0.86	2.26	3.072(4)	157
9	N12–H12a···O11^{ii}	0.86	2.31	2.957(4)	132

Equivalent positions: $^{ii}x, -y+1/2, z+1/2$; $^{iii}x, -y+1/2+1, z+1/2$; $^{iv}x, -y+1/2, z-1/2$; $^{v}-x+1, y-1/2, -z+1/2$; $^{vi}-x, y-1/2, -z-1/2$.

eight types of hydrogen bonds, listed in table 3 and numbered from 2 to 9, have been found. These bonds are important in the crystal organization, for which three following steps can be distinguished.

The first step is the polymer elongation in a linear fashion alongside crystallographic *b*-axis with sulfate bridges. The polymer chain is additionally stabilized by three hydrogen bonds (number 2, 3, and 4) formed by water, as illustrated in figure 2. In the second step, each water molecule provides the link between neighboring chains *via* H-bond number 5 (figure 3). The respective units of such pairs of chains as well as water molecules are related by the inversion center. The neighbor pair of chains is found at *c*/*2* crystallographic axis distance and its aromatic rings intercalate between similar rings of the first pair. The relative positions of the intercalating rings suggest attractive interaction between the ring π-electrons and respective hydrogens, as shown in figure 3. The shortest distances illustrating these interactions are found between ring centroids and H16 (2.851 Å) or H26 (3.136 Å). Due to non-parallel orientation of aromatic rings, next two similar distances are definitely longer (4.078 and 3.627 Å, respectively). The interactions are accompanied by much stronger hydrogen bonds formed between hydroxyl and sulfate (bonds number 6 and 7) or NH_2 (bonds number 8 and 9). There are no direct, or *via* water, interactions between polymer chains along the *a*-axis. They are linked indirectly *via* H-bonds number 6–9 and probably employ methanols which may randomly occupy the spaces between polymer chains.

3.2. *Vibrational spectroscopy*

The most interesting vibrations of metal complexes are those of the central metal. The best method for detecting such vibrations is a metal isotope technique, based on small differences between band positions measured for complex isotopologues prepared using a pair of different stable metal isotopes. Unfortunately, this method cannot be applied for cobalt complexes due to the lack of stable isotopes. However, another isotope effect can be used in the case of amine group coordination, because band wavenumbers related to metal–NH_2 vibrations show a clear downshift upon deuteration. Therefore, in the present investigation, the O,N-deuterated complex has been prepared and its IR

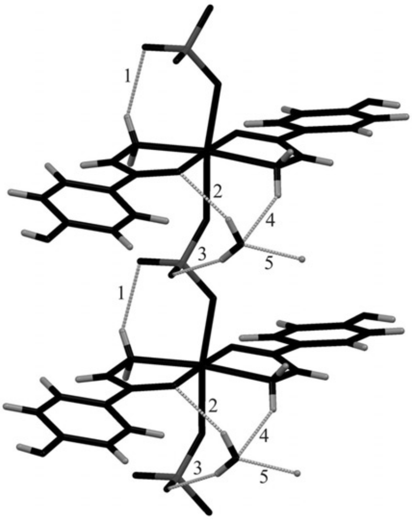

Figure 2. Fragment of polymer chain with accompanying water molecules.

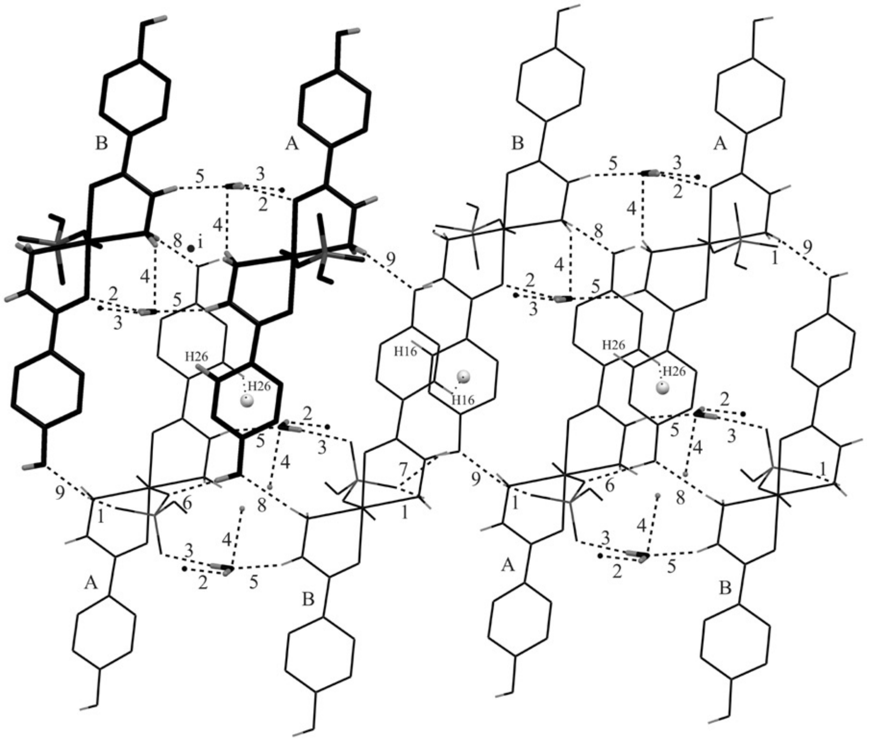

Figure 3. Hydrogen bonds with numbering listed in table 3.

spectrum is measured. Another method of detection and characterization of particular vibrational bands is based on calculations and modeling the molecular dynamics of the investigated compound. For this purpose, calculations have been carried out for the fragment of the polymer chain. The fragment is the same as that shown in figure 2, except for water molecules. Such choice provides a good model of the vibrations of the cobalt coordination sphere, as well as sulfate, acting in bidentate bridging mode (when only central SO_4 group, shown in figure 2, will be taken into account). The computed normal vibrations correlated with observed IR and Raman bands are presented in table 4. Comparison of the Raman and IR spectra for both natural and deuterated complexes in the 1800–100 cm^{-1} region is shown in figure 4.

3.2.1. Metal–ligand vibrations. The structure of cobalt suggests that the following metal–ligand stretching vibrations should be expected: $Co{-}NH_2$, Co–O(carbonyl), and Co–O(sulfate).

Calculations predicted a significant contribution of $\nu_s(Co{-}NH_2)$ internal mode in one theoretical band at 437 cm^{-1}. For deuterated molecule this band was computed at 410 cm^{-1}. Comparing the 400–500 cm^{-1} region in the IR spectra of natural and deuterated complex, only the 432 cm^{-1} band was found with similar wavenumber downshift, which pointed at it as a candidate for discussed mode. The corresponding $\nu_a(Co{-}NH_2)$ is strongly coupled with other internal modes, but its significant contribution has been found in the 550 and 527 cm^{-1} theoretical bands where the δ(O2–S–O4) and π(NH) also contribute. The last contribution makes these bands slightly affected by deuteration, which was also found for corresponding measured IR bands at 566 and 544 cm^{-1}.

The stretching vibrations of coordination bonds formed by metal and carbonyl group also split into asymmetric and symmetric modes. Such motions have been detected in calculated bands with 460 and 330 cm^{-1} maxima, respectively. In both modes, the stretch is mainly caused by motion of oxygen. However, the asymmetric stretch was also noted for normal modes at about 210 cm^{-1}, where the metal is mainly displaced along the O12–Co–O22 line.

The stretching vibrations of bonds linking metal and sulfate oxygens are obviously coupled with some deformation modes of SO_4^{2-}. It can be easily noticed in figure 2, when vibrations of coordination bonds formed by central sulfate are considered. The symmetric stretching must be accompanied by the bending of respective O1–S–O3 angle, whereas during the asymmetric stretching vibration the libration of whole SO_4 is expected. Such couplings cause the symmetric ν_s(O1–Co–O3) to be found at higher wavenumbers (calculated at 550 and 527 cm^{-1}) than corresponding asymmetric vibration (calculated at 381 cm^{-1}).

3.2.2. Sulfate group vibrations. The dynamics of sulfate is partially determined by coordination and hydrogen bonds in which this group participates. The atom displacements in respective normal modes indicate that the vibrations of S–O1 and S–O3 are mainly related to theoretical bands at 795 and 687 cm^{-1}. First band can be characterized as ν_a(O1–S–O3), whereas the second as ν_s(O1–S–O3) coupled with symmetric stretching vibration of two remaining sulfur–oxygen bonds, ν_s(O2–S–O4), which together resembles the totally symmetric vibration of an ideal tetrahedron. The vibrations of S–O2 and S–O4 are additionally differentiated by hydrogen bonds formed

Table 4. Wavenumbers and assignment of observed and calculated bands in vibrational spectra of $\{[\mathrm{Co(4hbah)_2}(\mu\text{-}\mathrm{SO_4})]_n \cdot \mathrm{H_2O} \cdot \mathrm{CH_3OH}\}_n$.

Observed			Calculated		
	IR				
Raman	H	D	H	D	Band assignment[a]
	3645	2700	–	–	[ν(CH$_3$O–H)][d]
n.o.	3545	2623	3710	2700	ν(OH)/ν(OD)[b]
n.o.	3301	2476	3641	2671	ν(NH)/ν(ND)
n.o.	3192	2458	3190	2354	ν_{a}(NH$_2$)/ν_{a}(ND$_2$)
3061	n.o.	n.o.	3119	3119	ν(CH)
n.o.	3192	2350	2880	2110	ν_{s}(NH$_2$)/ν_{s}(ND$_2$)
1648	1649	1186	1686	1231	δ(NH$_2$)/δ(ND$_2$)
n.o.	1649	1186	–	–	[δ(H$_2$O)/δ(D$_2$O)][d]
1611	1610	1608	1663	1661	ν(8 b)[c]
1569	1575	1569	1622	1615	ν(C=O) − ν(C–C) + ν(8 b)[c]
n.o.	1555	1557$_{\mathrm{sh}}$	1543	1544	ν(19 a)[c] + ν(C–N)
1506	1514	1470	1514	1462	ν(C–N) + ν(N–N)
1449	1446	1456	1454	1446	ν(19 b)[c]
1343	1347	–	1340	–	δ(NH) + ν(C–C) + [δ(CH$_3$O–H)][d]
1314	1317	975	1297	970	ρ_{t}(NH$_2$)/ρ_{t}(ND$_2$)
1298	1288	1282	1260	1253	ν(C–OH) + ν(8 a)[c]/ν(C–OD) + ν(8 a)[c]
1281	1275	1272	1254	1251	ν(8 a)[c] + ν(C–OH)/ν(8 a)[c] + ν(C–OD)
1244	1244	932	1313	965	ρ_{w}(NH$_2$)/ρ_{w}(ND$_2$)
1216	1214	1218	1214	1210	δ(CH)
n.o.	1184	919	1176	914	δ(OH)
1180	1165	919	1166	912	δ(OH) + ν(1)[c]/δ(OD)
1138	1135	1133	–	–	[ρ_{r}(CH$_3$)][d]
1098	1088	1096	896	896	ν(S=O2)
1038	1041	1046	807	806	ν(S=O4) − ν_{s}(O1–S–O3)
n.o.	1031	n.o.	795	806	ν_{a}(O1–S–O3)
978	975	975	687	692	ν_{s}(O1–S–O3) + ν_{s}(O2=S=O4)
1010	1008	n.o.	–	–	[ν(CH$_3$–OH)][d]
–	–	1005	–	1000	δ(ND)
895	896	860	902	876	ν(1)[c] + δ(OCN)
n.o.	858	860	848	852	π(CH)
770	763	760	758	761	τ(4)[c]
n.o.	740	610	756	572	ρ_{r}(NH$_2$)/ρ_{r}(ND$_2$)
n.o.	684	651	659	651	δ(6 b)[c]
638	633	633	620	618	δ(6 a)[c]
n.o.	596	–	549	–	π(NH) + δ(O2–S–O4)
n.o.	566	537	550	537	ν_{a}(Co–NH$_2$) + δ(O1–S–O3) + π(NH) + ν_{s}(O1–Co–O3)
541	544	524$_{\mathrm{sh}}$	527	515	δ(O1–S–O3) + ν_{a}(Co–NH$_2$) + π(NH) + ν_{s}(O1–Co–O3)
460$_{\mathrm{sh}}$	462	465	460	450	ν_{a}(Co–OC) + τ(16 a)[c]
425	432	415	437	410	ν_{s}(Co–NH$_2$) + δ(SO$_4$)
362	371	362	381	376	ν_{a}(O1–Co–O3) + lib(SO$_4$)
n.o.	596	596$_{\mathrm{sh}}$	353	353	δ(O2–S–O4)
330	333	327	330	330	ν_{s}(Co–OC) + δ(CNN)
247	248	246	241	240	lib(SO$_4$) + δ(Co–OS)
196	192	200	–	–	Lattice

[a] ν_{a} – Asymmetric stretching, ν_{s} – symmetric stretching, δ – bending in-plane, ρ_{t} – twisting, ρ_{w} – wagging, ρ_{r} – rocking, π – bending out-of-plane, τ – torsion, s – strong, m – medium, w – weak, vs – very strong, vw – very weak, sh – shoulder n.o. – not observed.

[b] The slash separates the assignment for natural and deuterated compound.

[c] Wilson's notation for benzene vibrations.

[d] Not calculated vibrations of water or methanol molecules.

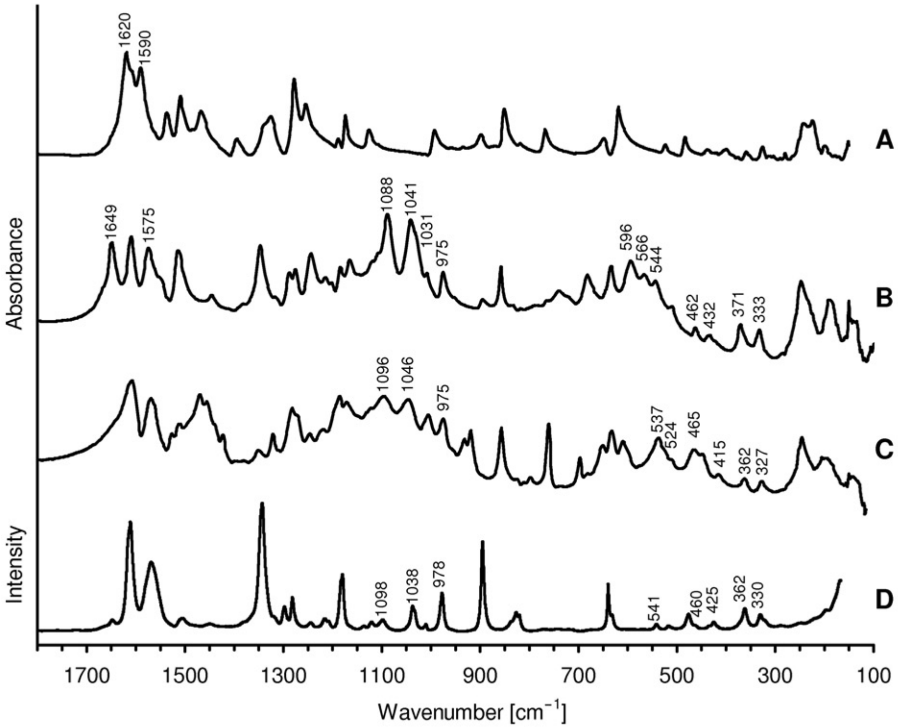

Figure 4. The 1800–100 cm^{-1} region in vibrational spectra of: **A** – ligand (IR), **B** – complex (IR), **C** – deuterated complex (IR), **D** – complex (Raman). Bands discussed in the article text are labeled.

with water and amine, respectively. The O2···H_2O bond is stronger which causes ν(S–O2) stretching mode to dominate the 896 cm^{-1} vibration. The O4···H_2N bond is weaker and corresponding ν(S–O4) mode contributes in the 807 cm^{-1} transition, together with ν_s(O1–S–O3) being out-of-phase. The bending vibrations of O1–S–O3 and O2–S–O4 subgroups are also separated by coordination and hydrogen bonds. The former is obviously coupled with symmetric stretching of Co–O1 and Co–O3, discussed above. The latter was calculated at 353 cm^{-1}. Comparison of both calculated and observed spectra suggests that sulfate group vibrations were underestimated in the applied computational model. The IR spectrum shows two very strong bands at 1088 and 1041 cm^{-1} and 1031 cm^{-1} shoulder which corresponds to three bands at 1170, 1105, and 1060 cm^{-1} observed for binuclear cobalt-ammine complex, where the sulfate group bridges [29]. These and remaining sulfate group vibrations published [29] were taken into account when computed frequencies presented above were correlated with observed bands, as listed in table 4.

3.2.3. Organic ligand vibrations. Apart from the observation of new "metal–ligand" bands, metal coordination is commonly confirmed by frequency shifts of bands related to the ligand coordinating centers [30]. The wavenumbers of ν(C=O) and $\delta(NH_2)$ were compared with corresponding values measured for pure ligand [31]. Upon metal coordination ν(C=O) position changes from 1620 (ligand) to 1575 cm^{-1} (present complex), whereas the $\delta(NH_2)$ absorption is shifted in opposite direction from 1590 to 1649 cm^{-1}. These shifts are caused not only by metal bonding, but also by additional effects. In the case of $\nu(C{=}O)$ small change of corresponding normal mode character is observed – in pure ligand the $\nu(C{=}O)$ internal mode is slightly coupled with $\delta(NH_2)$, from DFT calculations [31]. Similar calculations performed here shows the coupling of $\nu(C{=}O)$ with ν(C–C) and aromatic ring 8 b mode (Wilson's notation [32]). For the $\delta(NH_2)$ vibration, the influence of hydrogen bonding should be taken into account, but quantitative measurement of this effect is difficult. The spectral changes discussed above can be visually traced on figure 4, where the pure ligand IR spectrum is compared with spectra collected for the complex.

As mentioned above, the aromatic ring vibrations were characterized applying the popular Wilson's notation [32] (table 4). This notation was constructed for the ideal benzene molecule, but can be applied for di-substituted benzene as in 4hbah. Despite the lower symmetry, the phases of atom displacements of most normal vibrations are the same as in corresponding modes of benzene – only displacement amplitudes are frequently different. Since the aromatic ring is located away from metal coordination center, discussed vibrations are often similar to those of pure ligand [33] or other complexes [12, 33].

Supplementary material

CCDC 792544 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK: Fax: (+44) 1123-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

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