Synthesis, Crystal Structure and Vibrational Spectrum of Cobalt(II)orotate Trihydrate, $[Co(C_5N_2O_4H_2) \cdot 3\,H_2O$

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Cobalt orotate trihydrate, $[Co(C_5N_2O_4H_2)]\cdot 3H_2O$, has been synthesized and its crystal structure determined. The title compound crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19) with $a = 771.5(2)$, $b = 788.9(7)$, $c = 1470.4(2)$ pm, and $Z = 4$. Bridging orotate anions coordinate in a mono- and bidentate manner to the Co atom resulting in infinite chains of alternating Co(II) cations and orotate (OrH^{2-}) anions parallel to the *c* axis. The distorted octahedral Co coordination geometry is completed by three H_2O molecules. The FT-Raman and FT-IR spectra of the crystalline compound have been recorded and an assignment of the vibrational modes is proposed. The thermal behavior (TG) was investigated.

Key words: Cobalt(II)orotate Trihydrate, Crystal Structure, Vibrational Spectrum, Thermal Behavior

Introduction

Besides being biologically important [1 – 3] orotic acid (OrH_3) and orotate anions, respectively, may act potentially as mono- and bidentate complex ligands in aqueous solutions in the pH range up to about pH 10. Metal cations can be coordinated in several fashions *via* the carboxyl group, and the imino (-NH) functionalities as well as *via* the carbonyl groups (Fig. 1). H-bridge bonding is also involved. So far, nine different coordination motifs have been found [3]. Quite a couple of metal-orotate complexes, mostly with 3d-transition metals, were synthesized and characterized by X-ray crystal structure determination [1, 2, 4 – 10]. Vibrational spectra, especially Raman spectra, of metal orotates are scarce (*c.f.* discussion). With this investigation an attempt was started to characterize metal orotates by Raman spectra (in connection with crystal structure determinations), which can be recorded quickly and directly from the compound without suspecting changes by chemical reactions or phase transformation during sample preparation as it is the case for the IR (pellet) spectra. A further goal is the finding of specific metal related vibrational modes to get hints for the respective coordination as well as for the metal-orotate interaction.

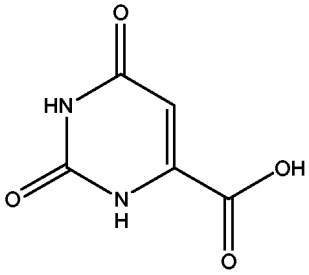

Fig. 1. Molecular structure of orotic acid.

X-ray structure analysis

A suitable single crystal of the title compound was selected under a polarization microscope and mounted in a glass capillary ($d = 0.2$ mm). Scattering intensities were collected with a single crystal diffractometer (STOE & CIE) using graphite monochromated Mo-K_α radiation (0.71073 Å). With the help of direct methods [11, 12] the atomic positions of Co, O, N, and C could be determined by successive refinement with Fourier syntheses including displacement parameters. The H positions were determined by final difference Fourier syntheses. For preparation of the structure drawings the programs SCHAKAL [13], STOP97 [14] and POV-Ray^{TM} [15] were used. Crystallographic details are summarized in the Tables 1 – 3.

Table 1. Crystallographic data and structure refinement of $[Co(C_5N_2O_4H_2)] \cdot 3\ H_2O$.

Empirical formula	$C_5N_2O_7H_8Co$
Formula weight [g mol^{-1}]	266.93
Crystal size [mm^3]	$0.20 \times 0.15 \times 0.20$
Crystal system	orthorhombic
Space group / Z	$P2_12_12_1$ (no. 19) / 4
a [pm]	771.5(2)
b [pm]	788.9(7)
c [pm]	1470.4(2)
Cell volume [10^6 pm^3]	894.9(3)
ρ_{X-ray} [g cm^{-3}]	2.082
μ [cm^{-1}]	2221
$F(000)$	556
Diffractometer	STOE IPDS, Mo-K$_\alpha$, $\lambda = 0.71073$ oriented graphite monochromator
Absorption correction	numerical, crystal description with 6 faces, shape optimized with X-SHAPE
Temperature [°C]	−103.2
2θ-Range [°]	$2\theta < 52.0$
Index-range	$-8 \le h \le 9$ $-9 \le k \le 9$ $-18 \le l \le 18$
No. of reflections, $R_{int.}$	6965, 0.0351
No. of independent reflections	1737
No. of parameters	168
Flack-X-parameter	−0.001(17)
Program	SHELX97
$R(I > 2\sigma_I)$, $wR(I > 2\sigma_I)$,	0.0233, 0.0641
R (all reflections), wR (all reflections)	0.0246, 0.0644
GooF	1.120
Largest difference peaks and hole	0.564 / −0.295

Table 2. Selected bond distances [pm] and bond angles [°] with e. s. d. in parentheses for $[Co(C_5N_2O_4H_2)] \cdot 3\ H_2O$.

Co - O1	207.3(2)	⟨O1 - Co - O4	86.8(1)
Co - O3	208.5(2)	⟨O3 - Co - O2	90.4(1)
Co - O2	208.8(2)	⟨O3 - Co - N1	93.6(1)
Co - O4	209.9(2)	⟨O1 - Co - O3	93.8(1)
Co - N1	210.3(2)	⟨O3 - Co - O4	171.5(1)
Co - O5	213.1(2)	⟨O1 - Co - O2	174.0(1)

Raman and IR spectra

The presented FT-Raman spectrum of the crystalline title compound was recorded with a Raman module FRA 106 (Nd:YAG laser, 1064 nm, > 200 mW) attached to a Bruker IFS 66v interferometer. The corresponding FT-IR spectrum was obtained from a KBr and PE pellet, respectively.

Thermal behavior

The **T**hermal **G**ravimetric (TG) analysis of the title compound was performed in an atmosphere of flowing argon (50 ml/min) and with a heating rate of 5 K/min using a 951 Thermogravimetric Analyzer / TA Instruments.

Table 3. Intra- and intermolecular hydrogen-bridge bonding [pm] in $[Co(C_5N_2O_4H_2)] \cdot 3\ H_2O$.

O1 - O6	278.4(4)	⟨O1 - H11 - O6	172.0(2)
O1 - O7	280.1(2)	⟨O1 - H12 - O7	175.7(5)
O2 - O4	312.0(4)	⟨O2 - H12 - O4	170.3(4)
O2 - O5	284.5(9)	⟨O2 - H22 - O5	173.8(1)
O3 - O7	270.4(5)	⟨O3 - H31 - O7	157.5(5)
O3 - O6	279.2(3)	⟨O3 - H32 - O6	164.8(5)
N2 - O4	286.4(2)	⟨N2 - H2 - O4	160.0(2)

Experimental Section

A Co^{2+} solution ($CoCl_2 \cdot 6H_2O$, Merck, p.a.; 1 mmol, 30 ml) was added in 1:2 stoichiometry to an aqueous sodium orotate solution ($NaOrH_2$; 2 mmol, 30 ml, 60 °C), prepared from orotic acid monohydrate (Fluka, purum) and an equivalent amount of NaOH. The pink-red solution was boiled (10 min.) and filtered off. During standing at room temperature for some days red brown crystals of $[Co(C_5N_2O_4H_2)] \cdot 3H_2O$ were grown. The product was dried at 30 °C, it is weathering stable on air.

Results and Discussion

Crystal structure of $[Co(C_5N_2O_4H_2)] \cdot 3\ H_2O$

$[Co(C_5N_2O_4H_2)] \cdot 3H_2O$ crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19). The cobalt compound is isotypic to the corresponding nickel compound, $[Ni(C_5N_2O_4H_2)] \cdot 3H_2O$ [10]. As shown in Fig. 2, the crystal structure of the title compound consists of infinite polymeric chains of alternating Co^{2+}

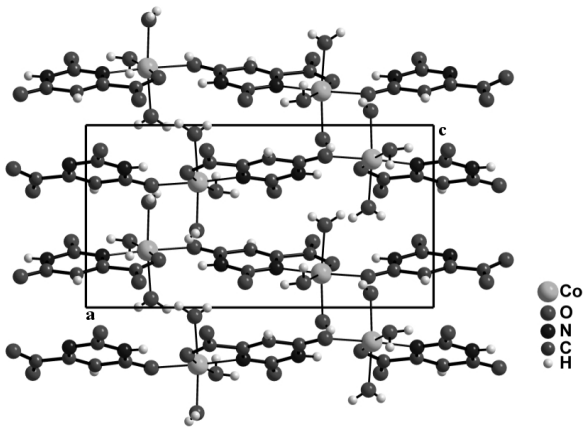

Fig. 2. Crystal structure of $[Co(C_5N_2O_4H_2)] \cdot 3\ H_2O$ along [010].

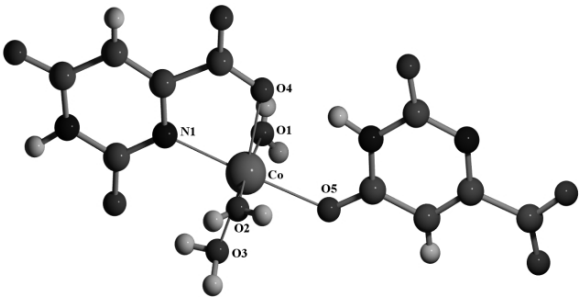

Fig. 3. Coordination of Co in $[Co(C_5N_2O_4H_2)]\cdot 3H_2O$.

cations and anionic orotate groups along the [001] direction.

The orotate groups coordinate in a monodentate manner *via* a carbonyl oxygen of the uracilate ring and in a bidentate manner *via* the nitrogen N1 and the carboxylate oxygen (Fig. 3). Three H_2O molecules complete the octahedral Co coordination which, therefore, is significantly distorted. All the hydrogen atoms of the H_2O molecules and those of the NH groups of the uracilate ring form hydrogen-bridge bonds. The Co-O distances are in the range of 207.3 to 213.1 pm and the Co-N distance amounts to 210.3 pm (Table 2).

The O···O distances in the O-H···O unit are in the range between 207.4 and 312.0 pm, and the O-H···O angles are in the range between 157.5 and 175.7° (Table 3). The found H-bridge-bond distances agree very well with those in $Na_2CO_3\cdot 1.5H_2O_2$ [16, 17]. The N···O distance of the N-H···O unit is 284.4(2) pm and the N-H···O angle 159.8(6)°. These values are comparable to those in ammonium compounds [18].

Vibrational spectroscopy

According to the crystal structure of the title compound its complex vibrational spectrum is dominated by the modes of the orotate group OrH^{2-} (Fig. 4, Table 4). Due to the low symmetry of the compound the corresponding IR and Raman bands were expected and found as in sodium and barium orotates [3, 19]. Very recently vibrational spectra of orotic acid [3, 8, 20], of the orotate anion, OrH_2^- [8 / Suppl. 4] and of a series of transion-metal orotates [3, 9, 10] were published along with assignments based on *ab initio* DFT (Density Functional Theory) calculations.

The changes upon formation of the Co(II) chelate compound can be followed by inspection and comparison of the vibrational spectra of orotic acid monohydrate [23] and of metal (Me^{2+}) orotates [3, 8 – 10], respectively, with the spectra of the Co(II) compound (*c.f.* Table 4). The orotic acid and orotate Raman and IR spectra are clearly separated in the two regions, one above 2800 cm^{-1}, representing the CH, N-H and

Table 4. Vibrational frequencies (cm^{-1}) of crystalline $[Co(C_5N_2O_4H_2)] \cdot 3\ H_2O$ along with their proposed assignments.

Raman	IR	Mode description[a]
	3468 vw, sh	ν $(H_2O)_{coord.}$
	3364 vw, sh	ν $(H_2O)_{coord.}$
	3305 vw, sh	ν $(H_2O)_{coord.}$
	3217 vs, br	ν $(H_2O)_{coord.}$
3136 w	3161 vw, sh	ν (N-H)
	3122 vvw	comb. band
3100 vw	3094 w	ν (C-H)
	3043 vw, sh	ν (C-H)
	2909 vvw, sh	and/or
	2809 m	comb. bands?
1719 vw, sh		comb. band?
	1704 vvs	ν $(C{=}O)_{carbox.}$
1660 vs		ν (C=O) + ν (C=C) + δ (H_2O)
	1641 vs	ν (C=O) + ν (C=C) + δ (H_2O)
1605 vw, sh	1613 vvw, sh	ν_{as} (COO^-)
1494 vw	1495 vvw, sh	Ur rg vibration
	1475 s	Ur rg vibration
	1425 vw	δ (N-H)
1410 m	1410 w	ν (Ur rg), δ (C-H)
1372 m	1380 vs	ν_s (COO^-)
	1303 w	δ (N-H)
1244 vs	1235 w-m	ν (Ur rg)
	1118 vvw	δ (C-H), Ur rg vibration
1053 vw	1037 w	δ (Ur rg)
1014 w	1014 vw	δ (Ur rg)
947 w		ν (Ur rg)
	931 vw	δ (N-H), Ur rg vibration
863 vw	860 w-m	γ (N-H), γ (C-H), γ (C=O)
801 vw, sh	801 w-m	γ $(C{=}O)_{carbox.}$ / δ (COO^-)
779 w-m	778 w-m	δ (COO^-) / γ $(C{=}O)_{carbox.}$
	754 w	γ (C=O), ρ (H_2O)
	718 vw	γ (C=O)
	691 vw	δ (C=O)
606 m	608 vvw	δ (Ur rg), δ (C=O), [ρ (H_2O)]
553 vw	548 vs	ν $(Co\text{-}OH_2)$, δ (Chel rg)
533 vw		ν $(Co\text{-}OH_2)$, δ (Chel rg)
	517 vvw	δ (Ur rg)
478 w	481 vvw	τ (Chel rg), τ (Ur rg), γ $(C{=}O)_{carbox.}$
	435 s	δ (C=O), δ (Ur rg)
424 vw		ν $(Co\text{-}OH_2)$
384 w		ν $(Co\text{-}OH_2)$
	238 m	δ (Chel rg), ν (Co-N), δ $(\text{-}O\text{-}Co\text{-}OH_2)$
203 vw		τ (Ur rg), τ (Chel rg)
	184 m	τ (Ur rg)
171 w		δ $(\text{-}O\text{-}Co\text{-}OH_2)$
102 vvs		τ (Chel rg), γ (OH_2)

Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad. [a] Notation: ν = stretching, δ = in-plane bending, γ = out-of-plane bending, τ = torsion, ρ = H_2O deformation, Ur rg = Uracilate ring, Chel rg = Chelate ring, carbox. = carboxylate.

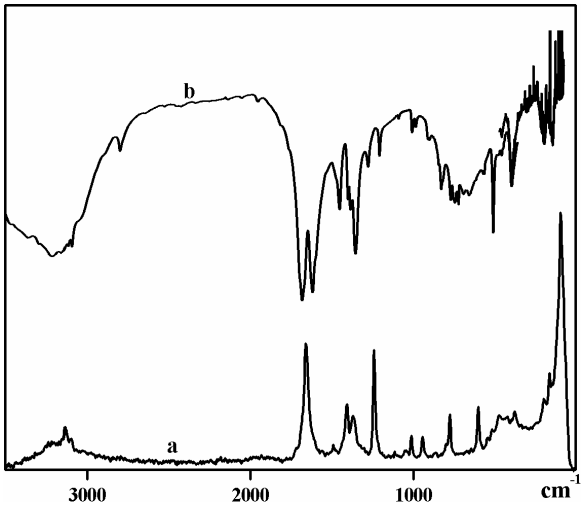

Fig. 4. FT-Raman ((a) // $\lambda_{exc.} = 1064$ nm) and FT-IR (b) spectra of crystalline $[Co(C_5N_2O_4H_2)]\cdot 3H_2O$ at room temperature. Raman intensity in arbitrary units; IR, transmittance.

H_2O stretchings, and the other mode rich range below 1750 cm^{-1}.

The C-H, N-H and H_2O stretching modes above 2800 cm^{-1} are seen and assigned respective to their expected frequency ranges [21, 22, 24] based on the *ab initio* calculations of orotic acid and metal orotates [8, 9, 20]. Complex vibrational coupling takes place in some vibrations in the frequency region below 1750 cm^{-1}.

By comparison of the known vibrational frequencies of a series of metal orotates [3, 8 – 10, 19] it can be concluded that some internal uracilate ring vibrations (*e.g.* 1495, 1476, 1014 and 947 cm^{-1}), as well as the N-H deformations at 1425 and 1303 cm^{-1} are almost unaltered upon complexation. On the other hand vibrational coupling takes also place for uracilate ring vibrations with δ(C-H) and δ(N-H) modes [δ(C-H) / ν(Ur rg): 1410 and 1118 cm^{-1}; δ(N-H) / Ur rg vibration: 931 cm^{-1}].

The carboxylate, -COO^-, formation/chelatisation is clearly indicated by ν_s (COO^-) around 1380 cm^{-1} (Raman: 1372 cm^{-1}, IR: 1380 cm^{-1}) in accordance with the frequency values of carboxylate formation generally and of that of comparable compounds [2, 3, 8, 21, 22, 24, 25]. The frequency range 1720 – 1600 cm^{-1} is dominated by very strong IR and Raman bands arising from C=O (carbonyl and carboxyl) and C=C stretchings according to the before mentioned *ab initio* calculations [8, 9, 20]. Additionally, the respective bands are very likely obscured by water bending modes. Since the carbonyl, carboxylate and C=C distances of the Co^{2+} orotate are nearly identical to those of nickel orotate pentahydrate, $Ni(OrH)\cdot 5H_2O$ [9] a similar mode assignment is proposed for the title compound. The sometimes mentioned ν_{as} (COO^-) mode for metal orotates is tentatively assigned to the very weak Raman and IR bands around 1610 cm^{-1} for the title compound. However, this vibration could also belong to the very strong IR band at 1641 cm^{-1}, or be hidden therein. Carbonyl and carboxyl bendings, often vibrationally coupled, have been settled in the 860 – 600 cm^{-1} range. Below 600 cm^{-1} the chelate ring bendings and vibrations of metal coordinated water as well as several ring torsions have been observed. The aforementioned modes appear around 550 cm^{-1} (Raman: 553 vw; IR: 548 vs). Obviously, a further mode-free region is seen between about 360 and 240 cm^{-1} in the Raman spectra of metal orotates [19]. It seems that metal specific differences/characteristics find their expression herein.

Thermal behavior

The thermal behavior of cobalt(II)orotate trihydrate was investigated from room temperature up to 800 °C. In the first distinct and endothermic step, beginning at round 140 – 150 °C, the three water molecules have been eliminated (calc. 20.24%, measured 20.77%) leaving the water-free cobalt(II)orotate. The intrinsic orotate decomposition in the succeeding step starting at round 300 °C does proceed dawdlingly ending up finally at around 550 °C. Surprisingly, only half of the cobalt content remained finally as cobalt oxide (CoO). Obviously, the thermal orotate decomposition is complex. The detailed decomposition mechanism is still unresolved.

It is also noteworthy that the thermal decomposition of $Ni(OrH)\cdot 5H_2O$ exhibits *via* $Ni(OrH)\cdot 3H_2O$ and Ni(OrH) striking similarities in comparison to that of the title compound [26].

Crystallographic data: Additional crystallographic data for the structure reported here can be obtained from the *Cambridge Crystallographic Data Centre* by quoting the depository number *CCDC* 254387, the names of the authors, and the journal citation.

Acknowledgements

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