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Phase relationships in cobalt iodate hydrates — thermal analyses, X-ray, IR, and Raman spectroscopic studies[☆]

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Abstract

The phase relationships of the cobalt iodate–water system have been examined using thermal analyses (DSC, TG), X-ray, IR and Raman spectroscopic methods. The compounds established are $Co(IO_3)_2{\cdot}4H_2O$, α-$Co(IO_3)_2{\cdot}2H_2O$, β-$Co(IO_3)_2{\cdot}2H_2O$, $Co(IO_3)_2$ as well as the novel compounds $Co(IO_3)_2{\cdot}xH_2O$ and $Co(IO_3)_2{\cdot}H_2O$. β-$Co(IO_3)_2{\cdot}2H_2O$ is isostructural to the respective nickel compound. $Co(IO_3)_2{\cdot}H_2O$ crystallises orthorhombic with a=827.18(6) pm, b=1104.52(8) pm, and c=772.26(4) pm. The vibrational spectra display acentric space groups (violation of the mutual exclusion principle) for $Co(IO_3)_2{\cdot}H_2O$ and $Co(IO_3)_2$. β-$Co(IO_3)_2{\cdot}2H_2O$ dehydrates to $Co(IO_3)_2$, $Co(IO_3)_2{\cdot}xH_2O$ at ~300 K (TG) to $Co(IO_3)_2{\cdot}H_2O$, and $Co(IO_3)_2{\cdot}H_2O$ at 519 K (DSC) to $Co(IO_3)_2$. Both the strength of the hydrogen bonds and the colour of the various cobalt iodate hydrates differ strongly. This is caused by the different ligand field splitting of the respective $Co(IO_3)_x(H_2O)_y$ polyhedra. The former is shown from the average wave numbers of the uncoupled OD stretching modes (isotopically dilute samples), which decrease in the range $Co(IO_3)_2{\cdot}H_2O$ (pale-pink, ν_{OD}: 2302 and 2248 cm^{-1}, 90 K)<α-$Co(IO_3)_2{\cdot}2H_2O$ (pink, ν_{OD}: 2453, 2423, and 2×2315 cm^{-1})<$Co(IO_3)_2{\cdot}4H_2O$ (wine-red)<β-$Co(IO_3)_2{\cdot}2H_2O$ (violet, ν_{OD}: 2519 and 2424 cm^{-1}).

Keywords: Cobalt iodate hydrates; Phase relationships; Raman and infrared spectra; X-ray powder data; Colour; Strength of hydrogen bonds

1. Introduction

Systematic studies on iodates and iodate hydrates of bivalent metals ([1–6] and further paper cited therein) resulted in detection of various hydrates and anhydrous salts, recording the infrared and Raman spectra, determining the crystal structures, investigation of the phase relationships and the thermal decomposition [4,5], ascertainment of the lone-pair radius of iodine(V) [3,4], detection of only incomplete intra-ionic coupling of the IO stretching modes [1,3] due to the distortion of IO_3^- ions in solid compounds [1–3], the distinction of IO_3 bending modes from MO stretching modes [5], and observation of unusual strong changes of the intensities of the respective Raman bands even in the case of isostructural series [6].

In the cobalt iodate–water system, $Co(IO_3)_2{\cdot}4H_2O$ [6,7], α-$Co(IO_3)_2{\cdot}2H_2O$ [8,9], β-$Co(IO_3)_2{\cdot}2H_2O$ [8,10], and $Co(IO_3)_2$ [7,11,12] have been reported in the literature, e.g., IR spectra of $Co(IO_3)_2{\cdot}4H_2O$

[☆] This work is dedicated to Prof. Harald Günther on the occasion of his 65th birthday.

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[8] and α-$Co(IO_3)_2{\cdot}2H_2O$ [8] and the crystal structures of α-$Co(IO_3)_2{\cdot}2H_2O$ [9], and $Co(IO_3)_2$ [12]. In a previous paper, we reported the vibrational spectra of α-$Co(IO_3)_2{\cdot}2H_2O$ [13] and the crystal structure and spectra of $Co(IO_3)_2{\cdot}4H_2O$ [6]. In this paper, we present the results of X-ray studies, IR, and Raman spectroscopic measurements, and thermal analyses especially of β-$Co(IO_3)_2{\cdot}2H_2O$ and $Co(IO_3)_2$, and of the new hydrates $Co(IO_3)_2{\cdot}xH_2O$ and $Co(IO_3)_2{\cdot}H_2O$. The existence of a sesquihydrate and a monohydrate has been already assumed by Maneva et al. [14] as a result of thermal analyses.

2. Experimental

2.1. Preparation

The compounds (as well as the deuterated specimens) studied, i.e. the various hydrates of cobalt iodate as well as the anhydrous salt, were prepared by crystallisation from aqueous solutions of iodic acid and cobalt nitrate as given below or by dehydration of the higher hydrates. The obtained precipitates were strained off, washed with ethanol and acetone, and dried in a desiccator.

Single crystals and polycrystalline samples of dark-wine-red $Co(IO_3)_2{\cdot}4H_2O$ and small crystals of pale-pink α-$Co(IO_3)_2{\cdot}2H_2O$ crystallise at temperatures below 4°C [6,7,15]. They can simply be separated by hand [15]. Violet β-$Co(IO_3)_2{\cdot}2H_2O$ crystallises at temperatures 30–70°C but mostly together with likewise violet anhydrous $Co(IO_3)_2$ [15,16]. Because manual separation was not possible we prepared pure samples of the dihydrate by dehydration at 80°C in a vacuum [15]. Pure samples of anhydrous $Co(IO_3)_2$ crystallise from boiling solutions at pH 5 [11,15].

Light-red polycrystalline samples of hitherto unknown $Co(IO_3)_2{\cdot}xH_2O$ were obtained by freezing in an acid solution with liquid nitrogen (in a similar way as for preparing $Ni(IO_3)_2{\cdot}10H_2O$ [5]). The frozen solution was then thawed in an refrigerator at −5°C within 10 h.

Pale-pink crystals of the monohydrate crystallise by interdiffusion of aqueous solutions of iodic acid and cobalt nitrate at ambient temperature within some days [15]. Two small preparation tubes filled with aqueous solutions of cobalt nitrate and iodic acid, respectively, were placed in a beaker and slowly flooded with distilled water. The colours of $Co(IO_3)_2{\cdot}H_2O$ and α-$Co(IO_3)_2{\cdot}2H_2O$ are very similar.

2.2. Apparatus and techniques

Differential scanning calorimetry (DSC) measurements were performed with 5–12 mg of the sample in a dry nitrogen stream using a Perkin–Elmer DSC 7 calorimeter with aluminium pans as sample holders. The heating rates were 5 and 10 K min^{-1}. An empty pan was used as reference. Thermogravimetry (TG) measurements were performed with the Mettler Toledo microbalance M3 and thermobalance TG 50 (nitrogen atmosphere, heating rate 10 K min^{-1}).

Raman spectra, with the samples in closed glass capillaries, were measured on a Bruker RFS100/S Fourier transform Raman interferometer (back-scattering geometry, 1064 nm line of a Nd:YAG laser) and on an Dilor multichannel Raman spectrograph (right-angle geometry, 647.1 nm line of an argon ion laser) (for the high-temperature measurements), respectively (resolution <4 cm^{-1}). For the low-temperature Raman spectra, the variable temperature cells Bruker model R495 were used. For high-temperature Raman spectra, a special high-temperature cell was used. More details on this cell and the temperature controlling system as well as on the measuring procedure of the high-temperature Raman spectroscopic studies are given elsewhere [5,17].

IR and FIR spectra were recorded on a Bruker IFS 113v model Fourier transform interferometer (resolution <2 cm^{-1}) using KBr discs, and fluorolub and nujol mulls as matrices. For low-temperature spectra (liquid nitrogen), the variable temperature cell Graseby Specac P/N 21.500 (with Eurotherm controller 808) was used.

X-ray powder diffractograms were recorded on a Siemens D5000 diffractometer in transmission geometry with primary monochromator and a Braun PSD-50M detector. X-ray Guinier photographs with the Huber 600 system using Cu Kα_1 radiation and α-quartz as an internal standard. Unit-cell dimensions and diffraction patterns were computed by the LSUCR [18] and VISUAL XPOW [19] programmes, respectively.

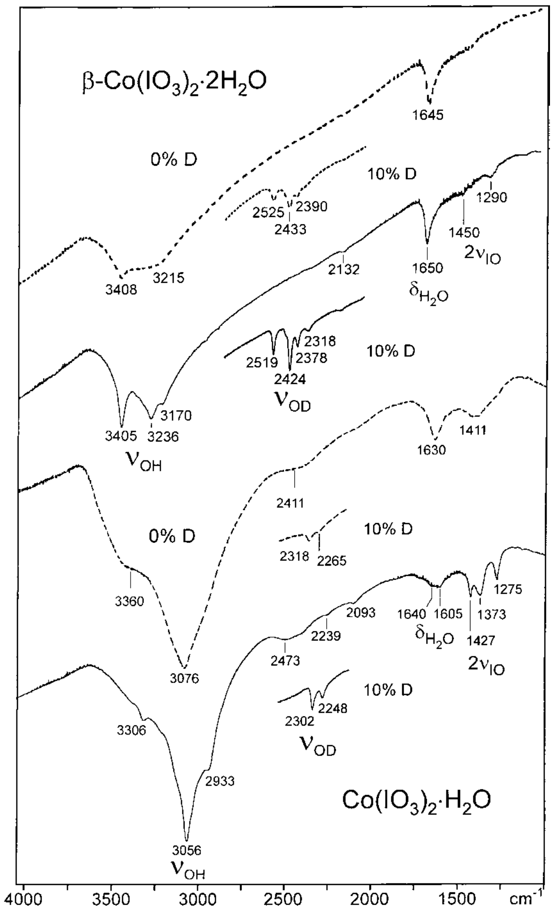

Fig. 1. Infrared spectra (KBr discs) of β-$Co(IO_3)_2{\cdot}2H_2O$ and $Co(IO_3)_2{\cdot}H_2O$ (0 and 10% D) in the ν_{OH}, ν_{OD} (OH and OD stretching modes), δ_{H_2O} (H_2O bending modes), and $2\nu_{IO}$ (two-phonon bands of IO stretching modes) mode region of the H_2O (and matrix isolated HDO) molecules and the IO_3^- ions (dashed line, 295 K; full line, 90 K; IR bands due to uncoupled OD stretching modes of α-$Co(IO_3)_2{\cdot}2H_2O$ [13] are 2453, 2423, 2315, and 2315 cm^{-1}; the respective Raman bands of β-$Co(IO_3)_2{\cdot}2H_2O$ being 2525, 2432, and 2365 cm^{-1} [15]).

3. Results

The compounds obtained and studied in this work are $Co(IO_3)_2{\cdot}xH_2O$, $Co(IO_3)_2{\cdot}4H_2O$, α-$Co(IO_3)_2{\cdot}2H_2O$, β-$Co(IO_3)_2{\cdot}2H_2O$, $Co(IO_3)_2{\cdot}H_2O$, and anhydrous $Co(IO_3)_2$. Infrared and Raman spectra of β-$Co(IO_3)_2{\cdot}2H_2O$, $Co(IO_3)_2{\cdot}H_2O$, and $Co(IO_3)_2$ are given in Figs. 1–5, those of $Co(IO_3)_2{\cdot}4H_2O$ and α-$Co(IO_3)_2{\cdot}2H_2O$ are reported in [6,13]. Structure data of $Co(IO_3)_2{\cdot}4H_2O$, α-$Co(IO_3)_2{\cdot}2H_2O$, and $Co(IO_3)_2$ are reported in [6,9,12], unit-cell dimensions of β-$Co(IO_3)_2{\cdot}2H_2O$ in [10]. In Table 1, *d*-spacings of $Co(IO_3)_2{\cdot}H_2O$ are given, those of other cobalt iodates will be transferred to JCPDS data file.

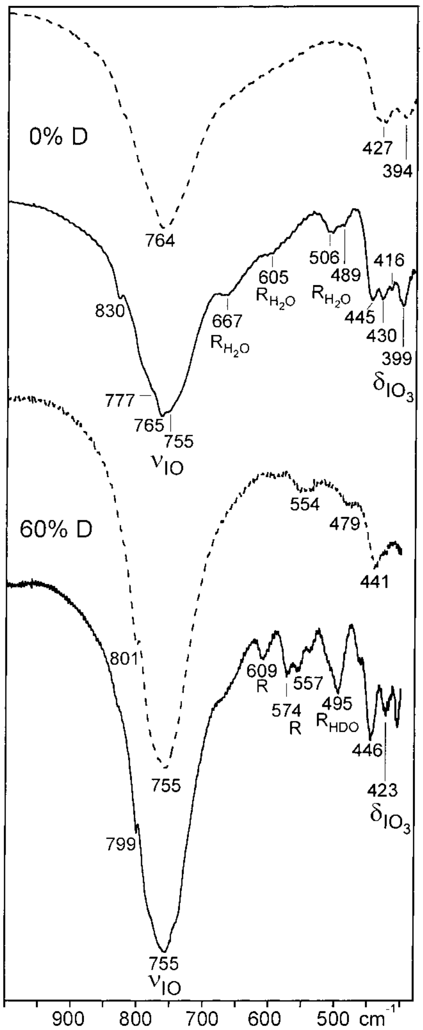

Fig. 2. Infrared spectra (KBr discs) of β-$Co(IO_3)_2{\cdot}2H_2O$ (0 and 60% D) in the 400–900 cm^{-1} range (ν_{IO}, δ_{IO_3}, IO stretching and IO_3 bending modes; R_{H_2O} and R_{HDO}, liberations of hydrate H_2O and HDO molecules, for further explanation, see Fig. 1).

3.1. Syntheses of cobalt iodates

The various hydrates of cobalt iodate can be crystallised from aqueous solutions at different temperatures and experimental conditions. Thus, dark-wine-red

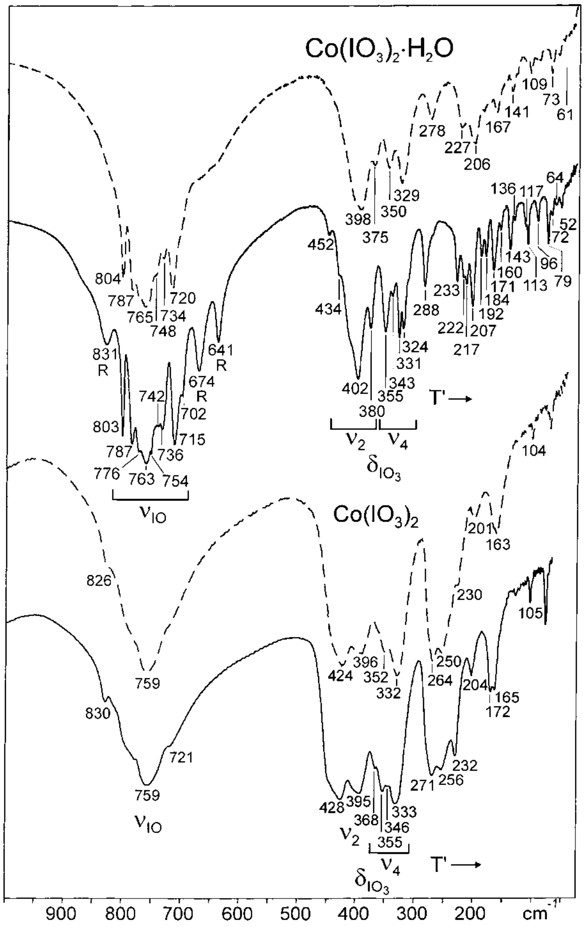

Fig. 3. Infrared spectra (KBr discs, nujol mulls on polyethene plates) $Co(IO_3)_2{\cdot}H_2O$ and $Co(IO_3)_2$ in the 400–900 cm^{-1} range (ν_2 and ν_4, IO_3 bending modes; *T*, translational modes, for further explanation, see Figs. 1 and 2).

$Co(IO_3)_2{\cdot}4H_2O$ and pink α-$Co(IO_3)_2{\cdot}2H_2O$ crystallise from aqueous solutions at <4°C beside one another [6,15], violet β-$Co(IO_3)_2{\cdot}2H_2O$ at 30–70°C [15], and violet anhydrous $Co(IO_3)_2$ at boiling [15]. β-$Co(IO_3)_2{\cdot}2H_2O$ and $Co(IO_3)_2$ can also be obtained by dehydration of higher hydrates [10,14].

The hitherto unknown hydrates $Co(IO_3)_2{\cdot}xH_2O$ and $Co(IO_3)_2{\cdot}H_2O$ were likewise obtained from aqueous solutions [15]. Thus, light-red $Co(IO_3)_2{\cdot}xH_2O$ and pink $Co(IO_3)_2{\cdot}H_2O$ were synthesised by freezing with liquid nitrogen and by interdiffusion of an aqueous solution of $Co(NO_3)_2$ and iodic acid, respectively. The true content of hydrate H_2O of $Co(IO_3)_2{\cdot}xH_2O$ could not be established.

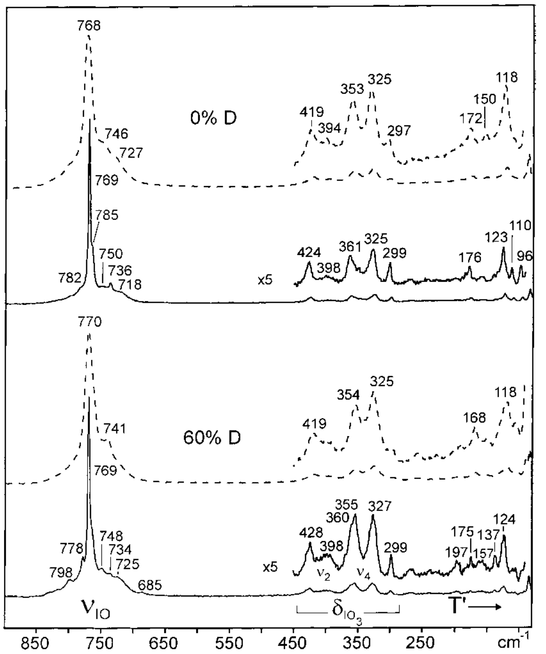

Fig. 4. Raman spectra of β-$Co(IO_3)_2{\cdot}2H_2O$ (0 and 60% D) in the 100–900 cm^{-1} range (for further explanation, see Figs. 1–3).

3.2. Crystal structures and spectra of cobalt iodates

$Co(IO_3)_2{\cdot}H_2O$ crystallises in the orthorhombic system with a=827.18(6) pm, b=1104.52(8) pm, and c=772.26(4) pm with four formula units in the unit cell. The IR and Raman spectra (see Figs. 1, 3 and 5) give no indication for an isotopism with other iodate monohydrates. The spectra display that the space group is probably acentric, i.e. the mutual exclusion principle is not fulfilled and that there are two hydrogen positions in the structure and probably two crystallographically different IO_3^- ions. The two uncoupled OD stretching modes (isotopically dilute sample), viz. 2302 and 2248 cm^{-1} at 90 K, reveal strong (for cobalt iodate hydrates) hydrogen bonds of this compound.

$Co(IO_3)_2{\cdot}xH_2O$ is decomposed on isolating forming the monohydrate. Therefore, X-ray data and vibrational spectra of this compounds could not be established. Nevertheless, it is a definite cobalt iodate hydrate different from the other compounds. Whether $Co(IO_3)_2{\cdot}xH_2O$ is identical with $2Co(IO_3)_2{\cdot}5H_2O$ [14] must be open for further investigation.

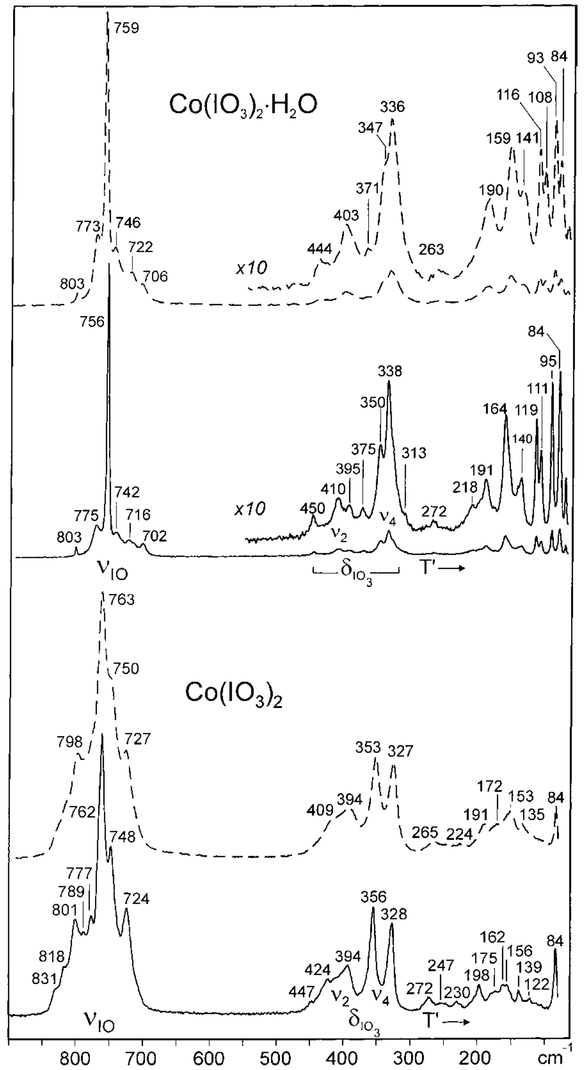

Fig. 5. Raman spectra of $Co(IO_3)_2 \cdot H_2O$ and $Co(IO_3)_2$ in the 50–900 cm^{-1} range (for further explanation, see Figs. 1–3).

β-$Co(IO_3)_2 \cdot 2H_2O$, which was firstly distinguished from the α-polymorph by Cordfunke [10], is isostructural to $Ni(IO_3)_2 \cdot 2H_2O$ [20]. The isotopism is confirmed by the IR and Raman spectra (see Figs. 1, 3 and 4) despite the relatively bad quality of the latter compared to the spectra of the nickel compound reported in [5]. Their crystal structures consist of isolated octahedral $M(IO_3)_4(H_2O)_2$ units, which are connected via relatively weak HO–H$\cdots$$OIO_2^-$ hydrogen bonds. The crystallographically equal hydrate H_2O molecules are distorted as shown from the wave numbers of the two uncoupled OD stretching modes(see Fig. 1). Like the isostructural nickel salt, there are weak additional OD stretching modes in the spectra of isotopically dilute samples (see Fig. 1). They possibly belong to an hitherto unknown hydrate.

Anhydrous $Co(IO_3)_2$ crystallises in the trigonal space group $P3$ [12] in contrast to most of the other anhydrous transition metal iodates (hexagonal space group $P6_3$, as $Mg(IO_3)_2$ [21] and α-$Li(IO_3)_2$ [22,23], or monoclinic, as β-$Ni(IO_3)_2$ [15], $Zn(IO_3)_2$) [13,24], and α-$Cu(IO_3)_2$ [25]). (β-$Ni(IO_3)_2$, which is monoclinic with a=540.1(1) pm, b=515.0(1) pm, c=539.2(1) pm and β=119.82(2)° [15] not hexagonal as reported in [5], is not isostructural to $Zn(IO_3)_2$ [13,25]).

The IR and Raman spectra of $Co(IO_3)_2$ (see Fig. 5) are compatible with two IO_3^- ions with C_3 and two with C_1 site symmetry in the primitive unit cell. For the IR and Raman spectra of β-$Ni(IO_3)_2$ and $Zn(IO_3)_2$, see [5,13].

3.3. Phase relationships, phase transition, and dehydration of cobalt iodates

The phase relationships of the cobalt iodate hydrates established by thermal analyses (DSC, TG, see Fig. 6) and high-temperature Raman spectra are given in Fig. 7. On dehydration of $Co(IO_3)_2 \cdot 4H_2O$, β-$Co(IO_3)_2 \cdot 2H_2O$ or directly anhydrous $Co(IO_3)_2$ are formed at 365 and 424 K (DSC data), respectively. The former as well as α-$Co(IO_3)_2 \cdot 2H_2O$ likewise dehydrate to $Co(IO_3)_2$. $Co(IO_3)_2 \cdot xH_2O$ dehydrates at ~300 K (via another route) to $Co(IO_3)_2 \cdot H_2O$, $Co(IO_3)_2 \cdot H_2O$ at 519 K to anhydrous $Co(IO_3)_2$. Hence, the dehydration temperature of $Co(IO_3)_2 \cdot H_2O$ is unusually high, which has not been observed in the case of other iodate hydrates with the exception of rare earth iodates as, for example, $Sc(IO_3)_3 \cdot H_2O$ with 543 K [26]. With the exception of β-$Co(IO_3)_2 \cdot 2H_2O$, all hydrates of cobalt iodate are obviously stable at distinct temperatures and H_2O partial pressures, even if they are not formed by dehydration of the tetrahydrate.

4. Discussion

4.1. Colour of cobalt iodates

The colour of the cobalt iodates under discussion varies between red, pink, and violet. The different

Table 1
Interplanar spacings *d* of $Co(IO_3)_2{\cdot}H_2O$ (in Å)

h	*k*	*l*	I/I_0	d_{exp}	d_{cal}	*h*	*k*	*l*	I/I_0	d_{exp}	d_{cal}
0	1	1	51.3	6.3382	6.3290	2	6	0	16.0	1.6816	1.6818
1	0	1	40.5	5.6408	5.6449	2	2	4	22.9	1.6677	1.6677
0	2	0	61.9	5.5207	5.52261	4	4	0	17.9	1.6553	1.6552
2	0	0	42.0	4.1341	4.1359	4	1	3	9.6	1.5946	1.5953
1	2	1	22.0	3.9510	3.9476	0	4	4	13.9	1.5822	1.5823
0	0	2	42.4	3.8599	3.8613	2	5	3	16.0	1.5537	1.5536
2	1	1	18.8	3.4605	3.4622	2	6	2	12.5	1.5424	1.5419
–	–	–	18.1	3.4351	–	4	4	2	13.2	1.5212	1.5213
2	2	0	100.0	3.3098	3.3105	5	1	2	9.7	1.5070	1.5064
0	2	2	77.5	3.1639	3.1645	3	6	1	9.8	1.5023	1.5018
2	0	2	43.0	2.8219	2.8224	2	4	4	16.3	1.4778	1.4778
0	4	0	24.2	2.7611	2.7613	2	7	1	13.2	1.4481	1.4481
2	3	1	19.8	2.5904	2.5906	0	3	5	10.0	1.4242	1.4243
1	3	2	15.3	2.5351	2.5362	4	0	4	12.2	1.4111	1.4112
2	2	2	34.3	2.5129	2.5132	5	4	1	9.8	1.3958	1.3958
1	4	1	13.4	2.4805	2.4804	0	8	0	10.7	1.3803	1.3806
1	0	3	11.6	2.4568	2.4579	4	2	4	14.0	1.3675	1.3673
3	2	1	11.6	2.3491	2.3499	2	3	5	12.4	1.3460	1.3467
2	4	0	12.2	2.2954	2.2965	6	2	6	13.7	1.3378	1.3376
1	2	3	23.7	2.2457	2.2456	5	5	0	10.2	1.3236	1.3242
3	3	0	10.8	2.2059	2.2070	3	2	5	10.2	1.3091	1.3091
0	5	1	13.4	2.1234	2.1239	6	0	2	13.6	1.2982	1.2984
0	3	3	11.6	2.1084	2.1097	4	6	2	14.0	1.2959	1.2953
4	0	0	22.7	2.0677	2.0679	0	0	6	11.3	1.2871	1.2871
2	4	2	42.0	1.9736	1.9738	2	7	3	12.1	1.2794	1.2793
4	2	0	14.6	1.9367	1.9366	2	6	4	13.3	1.2679	1.2681
0	0	4	16.4	1.9312	1.9306	6	2	2	13.2	1.2642	1.2639
2	5	1	15.9	1.8894	1.8893	4	4	4	13.9	1.2567	1.2566
5	2	?–	9.8	1.8683	1.8679	0	2	6	12.0	1.2536	1.2535
1	1	4	10.0	1.8532	1.8535	2	0	6	11.7	1.2292	1.2290
1	4	3	10.1	1.8355	1.8359	3	4	5	11.9	1.2111	1.2110
0	2	4	21.9	1.8226	1.8225	1	8	3	10.5	1.2039	1.2037
2	0	4	15.1	1.7495	1.7494	2	2	6	12.5	1.1998	1.1996
4	2	2	29.4	1.7310	1.7311						

colours of these compounds are obviously caused by the specific co-ordination polyhedra of the Co^{2+} ions and the different donor strength of the H_2O and IO_3^- ligands. Hence, a detailed study of the UV/VIS spectra of these compounds is recommended, when the crystal structures of all compounds are known.

4.2. Strength of hydrogen bonds

The strength of the hydrogen bonds present in the various cobalt iodate hydrates differ strongly ranging as $Co(IO_3)_2{\cdot}H_2O > \alpha\text{-}Co(IO_3)_2{\cdot}2H_2O > Co(IO_3)_2{\cdot}4H_2O > \beta\text{-}Co(IO_3)_2{\cdot}2H_2O$. This is shown from the different mean values of the OD stretching modes in the spectra of isotopically dilute samples, viz. 2275, 2376, 2407, and 2472 cm^{-1} (data from this work (Fig. 1) and from [6], and the respective H···O and O···O distances as far as known. At the first glance, this matter of fact is strange because probably in all these hydrates only $HOH{\cdots}OIO_2$ hydrogen bonds are formed, i.e. the same hydrogen bond donor and hydrogen bond acceptor each.

Both donor strength and acceptor capability of hydrogen bond forming entities, however, are modified by co-operative, synergetic, and competitive effects [21,27,28]. Hence, the donor strength of H_2O ligands differ depending on the nature of the respective co-ordination polyhedron. Thus, the donor

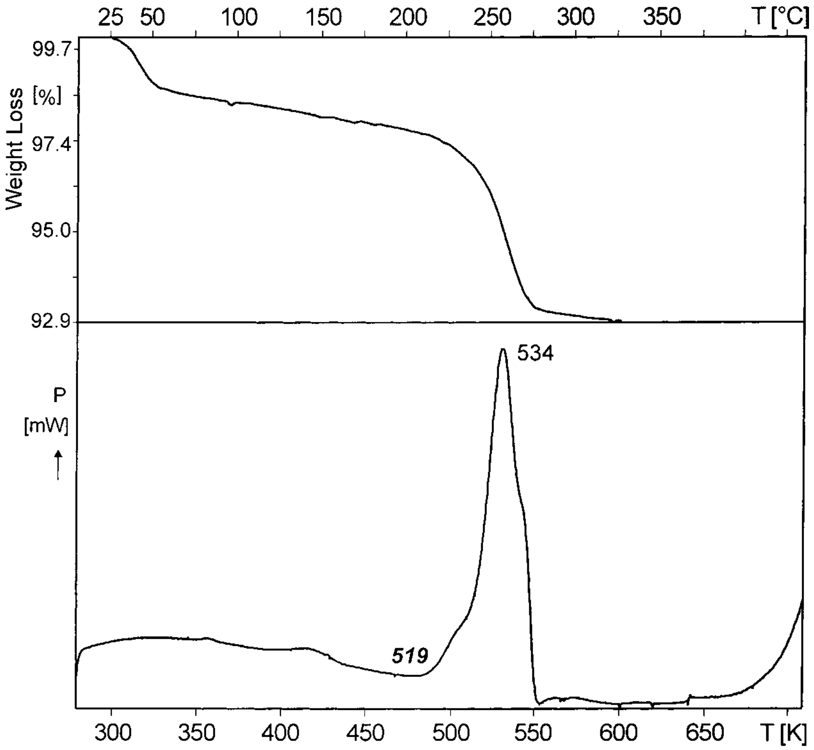

Fig. 6. DSC and TG diagrams of $Co(IO_3)_2{\cdot}H_2O$ (figures, temperatures (K) of intersection (italic), and peak maximum (roman)).

strength of hydrate H_2O molecules is greater in the case of $Co(IO_3)_4(H_2O)_2$ polyhedra (α-$Co(IO_3)_2{\cdot}2H_2O$) than in that of $Co(IO_3)_2(H_2O)_4$ ($Co(IO_3)_2{\cdot}4H_2O$). This is owing to the matter of fact that Co–OH_2 bonds are stronger than Co–OIO_2 bonds and, hence, the Co–OH_2 bonds of the diaqua complex are stronger than those of tetraaqua complex. The stronger the metal-oxygen bonds of the hydrate H_2O molecules, the greater is the hydrogen bond donor strength of the respective hydrate H_2O molecules. Similar considerations are possible with the competitive effect of the hydrogen bond acceptor capability of the iodate ions [28].

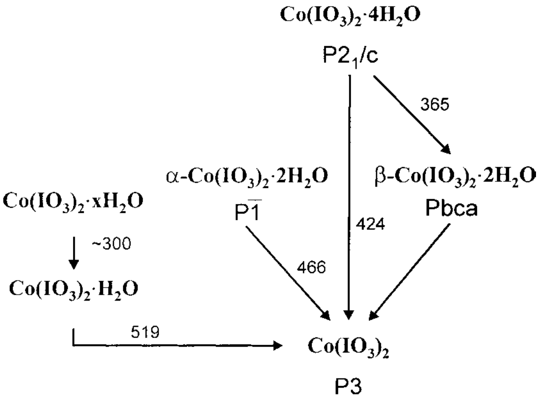

Fig. 7. Phase relationships of cobalt iodates (figures (K), transition temperatures (TG and DSC data)).

It is worth noting to mention that the relative strength of the hydrogen bonds formed in the various cobalt iodate hydrates correlates with the colours of the respective salts, which range as pale-pink, pale-pink, wine-red, and violet with decreasing strength of the hydrogen bonds. These findings are reasonable because the specific ligand field splitting influences both the colour of the salt and (via the different synergetic effect) the strength of the hydrogen bonds formed.

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