Preparation and study of phosphites. XXV.*
Bonding in cobalt(II) tetrahydrogentris(orthophosphite)

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Dedicated to Professor S. Škramovský on his 75th birthday

The cobalt(II) cations in cobalt(II) tetrahydrogentris(orthophosphite) $CoH_4(HPO_3)_3 \cdot 2H_2O$ are surrounded in the rather labile coordination sphere with the shape of a distorted octahedron by the oxygen atoms from two phosphite groups and two water molecules. An important role in the coordination sphere is played by hydrogen bonding between the water molecules themselves, between the water molecules and the anion with a bond length 0.281—0.305 nm, and in the $[H_4(HPO_3)_3]^{2-}$ anion itself with a bond length 0.257—0.265 nm.

В тетрагидротрис-ортофосфористокислом кобальте $CoH_4(HPO_3)_3 \cdot 2H_2O$ катионы Co(II) окружены в мало прочной координационной сфере формы деформированного октаэдра атомами кислорода, принадлежащими двум фосфитным группам и двум молекулам воды. Важную роль в связывающих отношениях координационной сферы играет водородная связь, которая образуется между молекулами воды взаимно, между молекулами воды и анионом — длина в пределах 0,281—0,305 нм —, и в самом анионе $[H_4(HPO_3)_3]^{2-}$ — длина в пределах 0,257—0,265 нм.

Cobalt(II) tetrahydrogentris(orthophosphite) was discovered during a solubility study in the $CoHPO_3$—H_3PO_3—H_2O system at 25°C [1], in the form of the trihydrate; it is a red-purple crystalline substance congruently soluble in water. The solubility diagram yielded rigorous conditions for its preparation, during which the initial trihydrate was converted into the dihydrate [1]. With the dihydrate, only the reflectance electronic spectra and the magnetic susceptibility have so far been studied [2], this leading to the conclusion that the cobalt(II) cation has a distorted

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octahedral coordination sphere. The ligand-field strength is lower than in cobalt(II) phosphite dihydrate, α,β-CoHPO$_3$ · 2H$_2$O [2], which verifies the assumption that the cobalt(II) cation is affected by the tris(orthophosphite) anion, which is bulkier than the phosphite anion.

In the present paper we describe a further study of the tris(orthophosphite) from the view-point of infrared molecular spectroscopy, thermography, and proton magnetic resonance. The stability of its aqueous solution to variations in the pH has been investigated. The aim was to obtain a more detailed picture of the bonding character in the coordination surroundings of the central cation.

Experimental

Chemicals and methods

Cobalt(II) tetrahydrogentris(orthophosphite) dihydrate, CoH$_4$(HPO$_3$)$_3$ · 2H$_2$O, was prepared according to the solubility diagram for the system CoHPO$_3$—H$_3$PO$_3$—H$_2$O [1] from a mixture of cobalt(II) phosphite, CoHPO$_3$ · 2H$_2$O, phosphorus acid, H$_3$PO$_3$, and water in the molar ratio of CoHPO$_3$:H$_3$PO$_3$:H$_2$O = 1 : 2 : 7.5. After equilibration, the pink-purple crystalline solid phase was filtered off, washed with ethanol and ether, and dried in the air. The results of the analysis of the substance obtained corresponded to the given formula. Cobalt was determined electrogravimetrically in an ammoniacal solution [3] and phosphorus gravimetrically as Mg$_2$P$_2$O$_7$, after the separation of cobalt as Co(OH)$_3$ and sample oxidation by triple evaporation with concentrated HNO$_3$. A partially deuterated substance, CoD$_4$(HPO$_3$)$_3$ · 2D$_2$O, was prepared by triple recrystallization from D$_2$O.

Infrared absorption spectra were obtained in nujol mulls and KBr pellets on a UR-20 instrument (Zeiss, Jena). The absorption bands were assigned using the spectra of the partially deuterated substance, CoD$_4$(HPO$_3$)$_3$ · 2D$_2$O.

Thermal decomposition was studied in the air at constant temperatures, increasing the temperature in 5—10°C steps to the attainment of a constant weight, and in an argon atmosphere, using a Derivatograph instrument [4] with a temperature gradient of 4.5°/min.

The magnetic susceptibility was measured by the Gouy method [5] at 77, 196, 273, and 298 K and magnetic field intensities of 0.18—0.45 T.

The proton magnetic resonance spectra were measured on polycrystalline CoH$_4$(HPO$_3$)$_3$ · 2H$_2$O and CoD$_4$(HPO$_3$)$_3$ · 2D$_2$O samples using a Tesla BS 477 spectrometer [6] at 15 MHz and 298 K. The spectra of the partially deuterated compound, CoD$_4$(HPO$_3$)$_3$ · 2D$_2$O were measured at 60 MHz and 193 and 298 K and at 15 MHz and 298 K. A modulation frequency of 15.4 Hz and a peak-to-peak modulation amplitude of 1—5 G were always employed. The high-frequency field amounted to ca. 0.1 G. In no case saturation was observed.

The amplified high-frequency signal was synchronously detected by a high-frequency synchronous detector and transmitted, after low-frequency amplification, to a low-frequency synchronous detector controlled by the field modulation generator. The low-frequency detector was directly coupled with a recorder or an electronic integrator.

A curve was constructed through the spectrum differential recording and 100—200 points were usually located on it. The absorption curve was obtained by numerical integration and the second moment of the spectrum was calculated. Although the proton magnetic resonance spectra of polycrystalline samples yield less information than the spectra of single crystals, owing to band overlapping and merging into a single broad band, data on the arrangement of atoms can still be obtained, chiefly from the spectral second moment. As the contributions to the second moment rapidly decrease with increasing distance, that of the closest atom is usually larger than the sum of all other contributions, which can be neglected to the first approximation. The spectra measured at various temperatures and magnetic field intensities permit the separation of the contributions from the electronic and nuclear magnetic moments of all atoms participating in interactions with protons [6]. If protons or proton pairs are equivalent, data on proton interactions can also be gained from the shape and asymmetry of the spectrum [7, 8]. Partial deuteration helps to distinguish groups of variously bonded protons.

During the study of the reaction of a cobalt(II) tetrahydrogentris(orthophosphite) solution with sodium hydroxide, a 0.5 M-NaOH solution was added from a burette to a 0.5 M-$CoH_4(HPO_3)_3 \cdot 2H_2O$ solution under continuous stirring with a magnetic bar; the pH was measured using an Acidimeter EK instrument (Druopta, Prague) with glass and the saturated calomel electrodes.

Results and discussion

Magnetic susceptibility and proton magnetic resonance

The values of the molar magnetic susceptibility corrected for diamagnetism and the effective magnetic moments are given in Table 1. Each magnetic susceptibility value is the average of nine experimental values at various magnetic field intensities. The temperature dependence obeys the Curie—Weiss law in the form $\chi_M = C/(T - \theta)$, the Weiss and Curie constants being equal to $\theta = -27$ K and $C = 2.972 \times 4\pi \times 10^{-6}$ K m^3 mol^{-1}, respectively.

The shape of the ^{1}H-n.m.r. spectra is given in Fig. 1 depicting selected spectra typical of $CoH_4(HPO_3)_3 \cdot 2H_2O$ and $CoD_4(HPO_3)_3 \cdot 2D_2O$. The similarity of the spectra at 193—298 K indicates that no substantial structural changes occur in this region and the water molecules are rigid even at room temperature.

The second moments of the spectra are given in Table 2; the values are the averages of 4—5 calculated values. The appropriate standard deviations are also given in Table 2, which also contains the time-averages of the electronic magnetic moments, $\bar{\mu}$, calculated from molar susceptibility χ_M. The susceptibility values at the given temperatures were calculated from the Curie and Weiss constants; no correction for diamagnetism was considered in this case.

The second moment of the resonance maximum for each hydrogen atom consists of several contributions

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Table 1

Molar magnetic susceptibility χ_M and effective magnetic
moment μ of $CoH_4(HPO_3)_3 \cdot 2H_2O$
The values are corrected for diamagnetism and their standard
deviations are given

T, K	298	273	196	77
$\chi_M \cdot (4\pi)^{-1} \cdot 10^9$ m^3 mol^{-1}	9.201±0.077	9.856±0.087	13.642±0.113	28.443±0.092
μ_{ef}, BM	4.69 ±0.03	4.64 ±0.03	4.61 ±0.03	4.14 ±0.01

Table 2

The second moment of resonance maxima $\langle\Delta H^2\rangle$ and the time-average of the electronic magnetic moment $\bar\mu$ of cobalt(II) ions in $CoH_4(HPO_3)_3 \cdot 2H_2O$ and $CoD_4(HPO_3)_3 \cdot 2D_2O$ in dependence on temperature T and magnetic field intensity H_0

Compound	H_0, 10^{-4} T	T, K	$\bar\mu$, 10^{-27} A m^2	$\langle\Delta H^2\rangle$, 10^{-8} T^2
$CoH_4(HPO_3)_3 \cdot 2H_2O$	14092	193	314.1	155.7±4
	14092	223	274.9	118.2±1.4
	14092	298	209.8	69.3±2.7
	3523	298	52.4	13.3±0.2
$CoD_4(HPO_3)_3 \cdot 2D_2O$	14092	193	314.1	69.8±6.1
	14092	298	209.8	39.5±1.1
	3523	298	52.4	6.5±1.6

$$\langle\Delta H^2\rangle = \frac{9}{5}\mu_H^2 \sum_i r_i^{-6} + \frac{4}{15}\sum_j \frac{I_j+1}{I_j}\mu_j^2\, r_i^{-6} + \bar\mu^2\left(\sum_p K_p\, r_p^{-3}\right)^2 \qquad (1)$$

where μ_H is the nuclear magnetic moment of the hydrogen atom (10^{-7} J G^{-1}) at distance r_i, I_j and μ_j are the nuclear spin and the nuclear magnetic moment of a non-resonating atom, respectively, and r_p is the distance of the paramagnetic ion. The K_p values depend on the position of the paramagnetic ions. If a single paramagnetic ion is close to the proton and interaction with distant ions is neglected, the last term in eqn (1) is simplified to 4/5 $\bar\mu^2\, r_p^{-6}$. The second moment may be somewhat higher for paramagnetic substances with non-spherical particles due to inhomogeneity of the magnetic field in the sample [7].

The second moments are plotted against $\bar\mu^2$ in Fig. 2. Extrapolating to $\bar\mu = 0$, the sum of the first two contributions in eqn (1) for the studied substance and its deuterated analogue is obtained, namely, 9.5×10^{-8} T^2 and 4.0×10^{-8} T^2, respec-
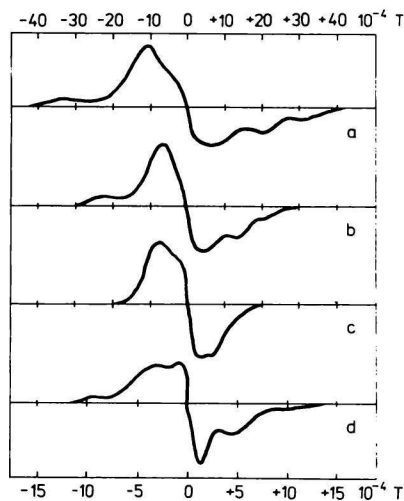
Fig. 1. Shapes of the ¹H-n.m.r. spectra.
a) $CoH_7P_3O_9 \cdot 2H_2O$ at 193 K and 60 MHz;
b) $CoH_7P_3O_9 \cdot 2H_2O$ at 298 K and 60 MHz;
c) $CoD_4H_3P_3O_9 \cdot 2D_2O$ at 298 K and 60 MHz;
d) $CoD_4H_3P_3O_9 \cdot 2D_2O$ at 298 K and 15 MHz.
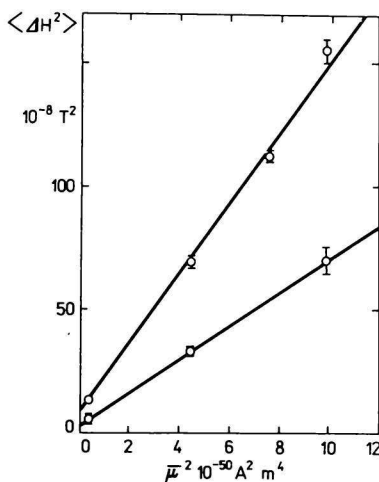The upper scale is valid for the first three curves.

Fig. 2. The values of the second moments of the spectral lines $\langle \Delta H^2 \rangle$ in dependence on the square of the average magnetic moment $\bar{\mu}^2$.

tively. All atoms with nuclear magnetic moments contribute to these values, *i.e.* ¹H, ²D, ³¹P, and ⁵⁹Co, whose contributions for a distance of 0.1 nm are 358.1×10^{-8}, 10.0×10^{-8}, 26.1×10^{-8}, and 188.2×10^{-8} T^2, respectively.

With the partially deuterated sample, the second moment is chiefly determined by the phosphorus atom, to which the proton is directly bonded. The other contributions barely exceed 0.5×10^{-8} T^2. The P—H distance is then obtained as 0.14 nm.

The value, 9.5 G^2, is, to a first approximation, the weighed mean of the second moments of the spectra of the three protons directly bonded to the phosphorus, four protons in the P—O—H groups, and four protons in the water molecules. The first contribution will be close to the second moment of the spectrum of the partially deuterated compound, $CoD_4(HPO_3)_3 \cdot 2D_2O$, at $\bar{\mu} = 0$, *i.e.* 4×10^{-8} T^2; in view of the higher magnetic moment of the hydrogen atom, its value was estimated to be 4.5×10^{-8} T^2. The last contribution is by far the largest, owing to the strong interaction of the close protons in the water molecule. The intermolecular contribution is substantially smaller; it always exceeds 2×10^{-8} T^2 in the hydrates so far studied. If this limiting value is also substituted for the second contribution, the distance between the protons in the water molecule is obtained as 0.1635 nm, corresponding to an intramolecular contribution of 18.75×10^{-8} T^2.

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The temperature correction leads to a decrease in this distance by several per cent [9].

The slopes of the straight lines given in Fig. 2 are determined by the distances and the positions of the paramagnetic ions. If only the effect of the closest ion is considered with the deuterated sample, the slope, $6.7 \times 10^{42}\ T^2 A^{-2}\ m^{-4}$, yields a Co—H distance of 0.326 nm. The Co—H distance in the coordinated phosphite group depends primarily on the dihedral angle and varies widely, from 0.30 to 0.44 nm, assuming that the P—O—Co angle equals $120°$ and the P—O and Co—O distances are 0.15 and 0.21 nm, respectively. The shape of the spectrum given in Fig. 1, however, indicates that the environments of the three protons are not identical.

The high value of the slope of the second straight line in Fig. 2, $13.9 \times \times 10^{58}\ G^4\ J^{-2}$, can only be explained by assuming that some protons are bound directly to the oxygen atoms in the first coordination sphere. If the contribution from these protons is assessed as $25 \times 10^{42}\ T^2\ A^{-2}\ m^{-4}$ (the average of the first four values in Table 3) and that of the others as $6.7 \times 10^{42}\ T^2\ A^{-2}\ m^{-4}$, then the value,

Table 3

The Co—H distance, r, and the slope of the straight line plot of $\langle \Delta H^2 \rangle$ vs. $\bar{\mu}^2$ for the coordinated OH group and the hydrogen bond to the coordinated oxygen atom

Structural motif*	r, nm	Slope $10^{42}T^2\,A^{-2}\,m^{-4}$
Co —0.20—0.21— O —120°— 0.10 —H	0.2646 / −0.2740	23.32 / −18.89
Co —0.20—0.21— O —109.5°— 0.10 —H	0.2517 / −0.2610	31.46 / −25.33
Co —0.21— O —120°— 0.17—0.18 —H	0.3297 / −0.3381	6.23 / −5.36
Co —0.21— O —109.5°— 0.17—0.18 —H	0.3111 / −0.3189	8.82 / −7.61

* Distances are given in nm.

4.3, is obtained for the number of close protons. For the sake of comparison, two cases involving hydrogen bonding when the oxygen in the first coordination sphere acts only as an acceptor are also included in Table 3; the slope is then substantially smaller and amounts to *ca.* 25—35% of the previous values. Even smaller values can be expected with hydrogen bonding to uncoordinated oxygen atoms. The macroscopic effects of magnetic field inhomogeneity, connected with the non-spherical particle shape, are also included in the slope value for the deuterated sample and thus do not affect the result.

It follows from the proton magnetic resonance spectra that no substantial structural changes occur within the temperature interval 193—298 K. The water molecules are not mobile and the average distance between their hydrogen atoms is larger than or at most equal to 0.163 nm. It follows from the dependence of the second moment of the spectra on the square of the time-average of the magnetic moments of the cobalt(II) cations that the four protons in the formula unit are directly bonded to the oxygen atoms in the coordination sphere. Both water molecules in the formula unit are therefore probably coordinated to the cobalt(II) cations. This interpretation is supported by the large proton—proton distance, which is common in coordinated molecules in which the valence angle is increased [10]. The polydentate phosphite groups are not bonded in the same way and thus probably belong to more cations. The analysis thus leads to the conclusion that the distorted octahedral coordination sphere of the cobalt(II) cation is formed by the oxygen atoms of the phosphite groups and the water molecules, the phosphite groups probably binding the coordination octahedra into a three-dimensional network similar to cupric phosphites [11, 12]. Phosphite anions also have a similar function in the LiH_2PO_3 crystal lattice [13].

Infrared molecular spectra, pH-metric titration,
and thermal analysis

The absorption band wavenumbers and band assignments are given in Table 4. In the spectrum analysis most attention was paid to in-plane deformation and stretching vibrations of the hydroxyl groups bound in the tetrahydrogentris(orthophosphite) anion and in the water molecules. It follows from the wavenumbers of the absorption bands that the crystal lattice involves a complex system of hydrogen bonds between the water molecules themselves, between the water molecules and the anion, and in the anion itself. On the basis of the dependence of the wavenumber of the hydroxyl group stretching vibration absorption band, $v(OH)$, and of the isotopic ratio, $v(OH)/v(OD)$ (1.43—1.31), on the hydrogen bond length [14—16], it was found that the hydrogen bonds in the anion are medium strong or strong with a length from 0.257 to 0.265 nm and those

Table 4

Infrared spectrum of cobalt(II) tetrahydrogentris(orthophosphite),
$CoH_4(HPO_3)_3 \cdot 2H_2O$

Wavenumber	Assignment	Wavenumber	Assignment
410 m		1205 sh	
475 m		1265 s	δ OH(POH)
505 w		1310 s	
545 s		1655 w	δ OH(H$_2$O)
570 sh		2400 m, b	ν OH(POH)
580 s	δ PO+γ OH+ρ H$_2$O	2440 m	
725 w		2460 m	ν PH+2δ OH(POH)
775 w		2480 m	
815 w		2900 m, b	ν OH(POH)
870 w		3400 s	
920 vs		3510 s	ν OH(H$_2$O)
1005 vs		3570 sh	
1040 vs		3600 sh	
1060 vs	ν PO+δ PH		
1095 vs			
1130 vs			
1170 vs			

vs — very strong, s — strong, m — medium, w — weak, b — broad, sh — shoulder.

involving the water molecules are weak with a length from 0.281 to 0.305 nm. The phosphite groups are thus bound in the lattice by a system of relatively strong hydrogen bonds which are a condition for the existence of the tetrahydrogentris-(orthophosphite) anion in the formula unit. The hydrogen bond energy was then determined for the water molecules according to *Yuchnevich* and *Karyakin* [17] as 7.5—23.4 kJ mol^{-1}. This wide energy interval for the hydrogen bonds involving the water molecules in the lattice is caused by polarizing effects of the cation and anion which, according to the *Samoylov* theory [18], lead to negative hydration of the anion and positive hydration of the cation [19].

The hydrogen bond system, which plays such an important role in the bonding interactions in the cobalt(II) cation coordination sphere, decreases the stability of the coordination sphere. This is verified by pH-metric titration of the cobalt(II) tetrahydrogentris(orthophosphite) aqueous solution with sodium hydroxide (Fig. 3), where the pink precipitate of the β-modification of cobalt(II) phosphite dihydrate, β-CoHPO$_3$ · 2H$_2$O [20], begins to separate after the first addition of hydroxide, and by the course of the thermal decomposition (Table 5), indicating that cobalt(II) tetrahydrogentris(orthophosphite) begins to dehydrate at 40°C and that anion oxidation begins at 140°C. Study of the thermal decomposition on the
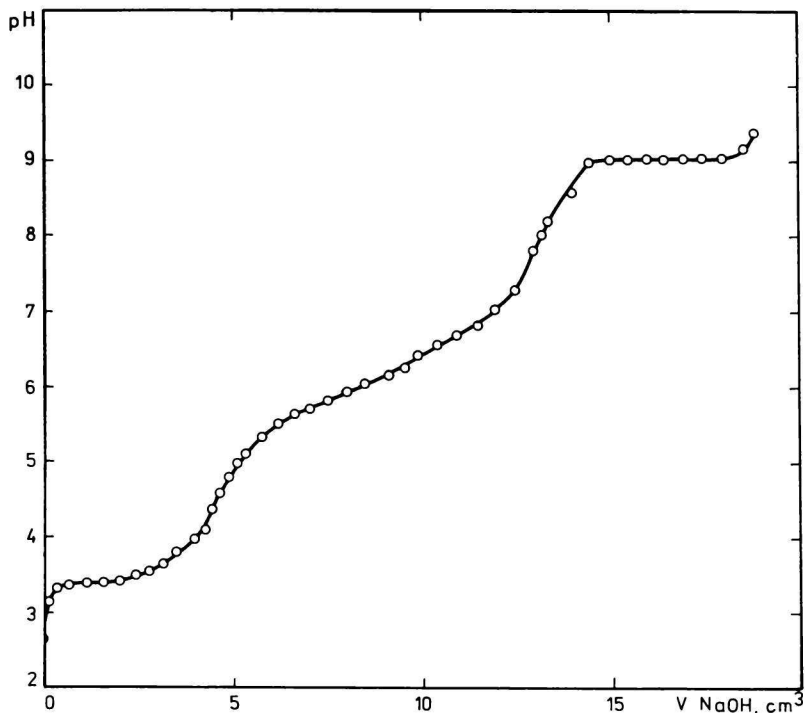
Fig. 3. pH-Metric titration of 5 cm³ 0.5 M-CoH$_4$(HPO$_3$)$_3$ · 2H$_2$O with 0.5 M-NaOH.

Table 5

Thermal decomposition of cobalt(II) tetrahydrogentris(orthophosphite),
CoH$_4$(HPO$_3$)$_3$·2H$_2$O

Method	T, °C	Effect
I	40	Beginning of dehydration
	140	Oxidation with partial dehydration
II	140	Beginning of dehydration
	165	Dehydration (—2H$_2$O)
	270	Oxidation

I — decomposition in the air with gradual increase in the temperature.
II — decomposition in an argon atmosphere on a Derivatograph instrument.

Derivatograph instrument shows a shift in the temperatures of all these effects to higher values, owing to different experimental conditions. The difference of 130°C observed in the oxidation-reduction decomposition is apparently also partially caused by the slow liberation of the water of hydration during gradual heating at a constant temperature [20—22].

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