STUDY OF CHROMIUM(II) PHOSPHITES*

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Chromium(II) phosphites $CrHPO_3.H_2O$, $CrDPO_3.2\,D_2O$, $CrH_4P_2O_6.H_2O$, and $CrD_4P_2O_6.D_2O$ were studied in the solid state by powder X-ray diffraction, thermography, electronic reflection spectroscopy, magnetic susceptibility measurements, and Raman and infrared absorption spectroscopy. The phosphite $CrHPO_3.H_2O$ involves an anion whose point symmetry is reduced from C_{3v} to C_s. The vibrational spectra of the phosphite $CrDPO_3.2\,H_2O$ were discussed in terms of the correlation and factor group approach. Chromium(II) dihydrogenbis(orthophosphite) involves in the crystal lattice two hydrogen bonds, lengths 269 ± 2 pm and 286 ± 2 pm. The stronger hydrogen bonding is originated on the interaction of an oxygen atom and a hydroxyl group bonded at two different phosphorus atoms, and brings about among others a lowering of the crystal field strength in the hydrogenphosphite. The weaker hydrogen bond is probably formed between the anion and the water molecule.

During the study[1] of the solubility in the system $CrHPO_3$–H_3PO_3–H_2O at 25°C the formation of a single hydrogenphosphite $CrH_4P_2O_6.H_2O$ has been established. The preparation of $CrHPO_3.H_2O$ and the deuterated phosphite $CrDPO_3.2\,D_2O$ isostructural with $CuHPO_3.2\,H_2O$ has been reported[2,3].

In the present work, various techniques were applied to the study of the structure of chromium(II) phosphites; emphasis was placed on the investigation of the hydrogen bonding in chromium(II) dihydrogenbis(orthophosphite), inasmuch as this is a characteristic building motive in the crystal lattices of hydrogen phosphites[4–9].

EXPERIMENTAL

The phosphorous acids H_3PO_3 and D_3PO_3 were prepared by reaction of phosphorous chloride with H_2O and D_2O, respectively. The phosphites $CrHPO_3.H_2O$, $CrH_4P_2O_6.H_2O$, and the deuterated phosphite $CrDPO_3.2\,D_2O$ were prepared as reported previously[1,3], the deuterated phosphite $CrD_4P_2O_6.D_2O$ was prepared, based on the conditions found from the study of the solubility diagram[1], by reaction of 1·3 g of $CrDPO_3.2\,D_2O$, 1·4 g of D_3PO_3, and 1·7 g of D_2O for six days. The compounds were analyzed gravimetrically and cerimetrically[1]. All the operations with the substances under study were performed in protective nitrogen atmosphere.

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The powder X-ray diffraction patterns were obtained by applying the Debye–Scherrer method on an instrument Mikrometa II (Chirana) with CuKα radiation. The sample was placed in a sealed Lindenmann capillary under nitrogen.

The thermal decomposition in nitrogen atmosphere was studied on an apparatus Derivatograph (MOM, Budapest) in the temperature region 298—873 K, with the temperature rise rate 5 K/min.

The magnetic susceptibilities were measured by the Faraday method in the Terry's modification[10]. The temperature dependence of magnetic susceptibility was studied by the Gouy method on an apparatus constructed by Julák[11].

The electronic reflection spectra were measured on an instrument VSU-2P (Zeiss, Jena). The infrared absorption spectra were scanned in the region 400—4000 cm^{-1} on a prism spectrophotometer UR 20 (Zeiss, Jena) by applying the KBr disk and nujol and tripene mull techniques. The Raman spectra were run on an instrument Jeol JRS-S1 equipped with an argon laser ($\lambda = 488$ or 514·5 nm), power 60—70 mW.

The samples were handled in a glove box during the study of their spectral and magnetic properties.

RESULTS AND DISCUSSION

X-Ray Diffraction Patterns

The powder X-ray diffraction patterns displayed the following lines (*d* values in nm/intensities in a relative ten-point scale): $CrHPO_3.H_2O$: 0·56/2, 0·46/5, 0·44/8, 0·42/1, 0·37/1, 0·320/10, 0·301/4, 0·280/5, 0·271/9, 0·259/9, 0·226/2, 0·221/4, 0·210/1, 0·197/6, 0·187/1, 0·183/7, 0·179/2, 0·168/9. 0·159/1, 0·154/2, 0·141/2, 0·136/2, 0·134/2, 0·127/1, 0·125/1.

Chromium(II) dihydrogenbis(orthophosphite): 0·51/7, 0·42/5, 0·343/6, 0·322/10, 0·312/4, 0·298/4, 0·257/4, 0·246/3, 0·239/3, 0·230/2, 0·219/1, 0·213/6, 0·199/5, 0·189/3, 0·183/2, 0·179/1, 0·173/3, 0·165/2, 0·161/5, 0·157/5, 0·150/5, 0·144/1, 0·139/1, 0·132/2, 0·128/2, 0·122/1, 0·118/1, 0·115/2, 0·1086/1, 0·1038/1, 0·0996/2.

These values indicate that the phosphites prepared are chemically uniform and that the crystal structures of $CrHPO_3.H_2O$ and $CrDPO_3.2\,D_2O$ (ref.[3]) are different.

Thermography

The course of the thermal decomposition with linearly increasing temperature in nitrogen atmosphere is given in Table I. The results for $CrHPO_3.H_2O$ indicate a complete dehydration of the sample in the temperature region 350—575 K, the oxidation–reduction decomposition only taking place at higher temperatures. The process of dehydration and the oxidation–reduction decomposition of the phosphite $CrDPO_3.2\,D_2O$ are analogously separated too. While the GTA curve of this substance does not display a plateau corresponding to the existence of $CrDPO_3.D_2O$, the formation of the latter can be traced on the DTA curve. This behaviour indicates close strengths of the bonds of the two D_2O molecules in the crystal lattice, although — in analogy to $CuHPO_3.2\,H_2O$ — they play different structural parts[3,12].

TABLE I

Thermal Decomposition of Chromium(II) Phosphites

Temperatures in K; the values in brackets give the weight loss in mol H_2O.

Data	$CrHPO_3 . H_2O$	$CrDPO_3 . 2 D_2O$	$CrH_4P_2O_6 . H_2O$
		DTA	
ENDO — start	475	365	510
		—	685
ENDO — minimum	570	425	535
		465	720
EXO — start	855	850	620
EXO — maximum	875	875	650
		GTA	
Start of dehydration	350	310	320
	575 [0·94]	575 [1·96]	475 [0·20]
			625 [1·16]
		DGTA	
GTA — inflexion	525	415	—
	605	465	535

TABLE II

Values of the Magnetic Susceptibilities χ_M, Magnetic Moments μ_{eff}, and Parameters $10Dq$ of the Chromium(II) Phosphites Studied

Compound	T K	χ_M $mm^3 mol^{-1}$	μ_{eff} B. M.	$10Dq$ mm^{-1}
$CrHPO_3 . H_2O$	77	413	4·50	—
	196	182	4·76	—
	273	129	4·73	—
	298	122	4·82	1 370
$CrDPO_3 . 2 D_2O$	298	—	—	1 370
$CrH_4P_2O_6 . H_2O$	298	127	4·91	1 310

Chromium(II) dihydrogenbis(orthophosphite) liberates one water molecule during its thermal decomposition. The formation of the diphosphite at higher temperature (found[8,13] with a number of bivalent metal dihydrogenbis(orthosphosphites)) is precluded in the case of the chromium(II) salt due to the oxidation–reduction decomposition at 620 K.

Magnetic Susceptibility and Electronic Reflection Spectra

The magnetic susceptibilities, magnetic moments, and the Dq values of the chromium(II) phosphites under study are given in Table II. The magnetic moment values are in accordance with the zero orbital contribution of the ^5E_g state in the octahedral crystal field and the low value of the spin-orbital interaction constant[14]. The value of the Weiss constant of $CrHPO_3.H_2O$ $\Theta = -10$ K emerged from the temperature dependence of the magnetic suceptibility. No antiferromagnetic interactions were evidenced in the temperature region 77 – 298 K, as in the case of other transition metal phosphites[5,6,8,15].

The electronic reflection spectra involve a single band ($^5T_{2g} \leftarrow {}^5E_g$), whose wavenumber equals the value 10 Dq, given in Table II. In the case of the phosphite $CrDPO_3.2\,D_2O$ the Jörgensen's parameter $f_{DPO_3^{2-}}$ could be determined for the chromophor $[Cr(D_2O)_3\,(DPO_3)_3]$, found by X-ray diffraction analysis[3,12]. Using the effective crystal field concept the value $f_{DPO_3^{2-}} = 0{\cdot}94$ was obtained, which compares well with the $f_{HPO_3^{2-}}$ values of other transition metal phosphites[15,16].

The bathochromic shift for chromium(II) hydrogenphosphite as compared with $CrHPO_3.H_2O$ is analogous to the case of iron(II)[8], cobalt(II)[15], and nickel[15] phosphites, and similarly as in the paper[8] can be interpreted as one of the possible consequences of the lowering of the electron density at the oxygen atom during its protonation and the hydrogen bond formation in the coordinated anion.

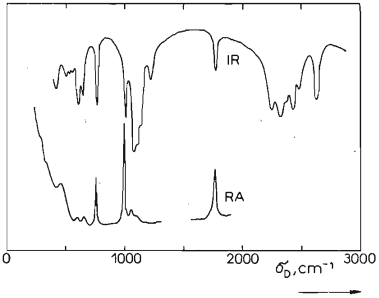

FIG. 1

Infrared and Raman Spectra of the Phosphite $CrDPO_3.2\,D_2O$

Vibrational Spectra

The infrared and Raman spectra of the substances studied and of their totally deuterated analogues are given in Tables III – V; the spectra of $CrDPO_3.2\,D_2O$ are reproduced in Fig. 1.

The spectra of the phosphite $CrHPO_3.H_2O$ can only be interpreted in the point group approach, because the space group of the substance is not known. A deformation of the phosphite anion is in this approximation characterized[17,18] by the force constants $k_{PO} = 790\ N\ m^{-1}$, $k_{PO_2} = 680\ N\ m^{-1}$, with the internuclear distances

TABLE III

Infrared Spectra of $CrHPO_3 . H_2O$ and $CrDPO_3 . 2\,D_2O$

The wavenumbers σ (cm^{-1}) pertain to the temperature 298 K, the wavenumbers σ' (cm^{-1}) to the temperature 77 K; in the assignemnt, H stands for D in the case of the deuterated compound. Relative band intensity: vs very strong, s strong, m medium, w weak, vw very weak; sh shoulder.

$CrHPO_3 . H_2O$		$CrDPO_3 . 2\,D_2O$		Assignment
σ	σ'	σ	σ'	
430 m	430 s	420 m	430 s	$\varrho(OPO) + \varrho(H_2O) + \gamma(HOH)$
485 m	495 m	505 m	510 m	
575 sh	565 sh	535 m	530 m	
630 s	630 s	560 m	560 m	
725 w	745 m	625 s	630 s	
		655 m	680 m	
1 030 vs	1 035 vs	765 s	770 s	$\delta(OPH)$
1 045 vs	1 050 vs			
1 000 s	1 005 s	1 010 s	1 010 s	$\nu_s(PO)$
1 075 vs	1 075 vs	1 080 vs	1 070 sh	$\nu_{as}(PO)$
1 105 sh	1 100 vs	1 090	1 085 vs	
1 130 sh	1 145 s	—	1 100 vs	
		1 125 sh	1 140 s	
			1 160 sh	
1 635 m	1 645 m	1 230 m	1 235 m	$\delta(HOH)$
2 460 m	2 465 m	1 775 m	1 780 m	$\nu(PH)$
2 950 sh	2 930 w	2 240 s	2 220 s	$\nu(OH)$
3 330 sh	3 350 sh	2 310 s	2 295 s	
3 460 vs	3 475 vs	2 350 sh	2 350 m	
		2 460 m	2 425 s	
		2 610 s	2 595 s	
3 200 sh	3 215 s	2 410 s	2 405 s	$2\delta(HOH)$

$r_{PO} = 148$ pm, $r_{PO2} = 151$ pm. These values are comparable with the parameters of the other transition metal[5,8,18] and non-transition metal[4,17,19] phosphites.

Making use of the published data[3,20,21], the vibrational spectra of $CrDPO_3.2\,D_2O$ can be interpreted based on the correlation and factor group analysis. The crystals of the substance belong to the space group $D_2^4 - P2_12_12_1$ ($Z_P = 4$), all atoms in a primitive elementary cell being localized in general fourfold positions. Each of the positions belongs in the factor group isomorphic with the point group D_2 (the space group D_2^4 is not symmorphic) to the modes $3(A + B_1 + B_2 + B_3)$, thus the total of the modes of the twelve atoms in $CrDPO_3.2\,D_2O$ corresponds to the representation $36\,(A + B_1 + B_2 + B_3)$. The division of these vibrational modes among the internal and external ones and their spectral activities are given in Table VI. The correlation of the internal vibrational modes of the DPO_3^{2-} and D_2O fragments are given in Table VII. However, not all of the theoretically expected bands have been found in the spectra, similarly as in the case of other phosphites[22]. The multiplication of the number of vibrations following from the factor group analysis appears

TABLE IV

Infrared Spectra of $CrH_4P_2O_6 . H_2O$ and $CrD_4P_2O_6 . D_2O$

Symbols used as in Table III; the subscripts H and D refer to the hydrogen and deuterium containing compounds, respectively.

σ_H	σ'_H	σ_D	σ'_D	σ_H/σ_D	σ'_H/σ'_D	Assignment
410 m	415 m	—	—	—	—	$\delta(OPO) + \varrho(H_2O)$
460 m	465 m	460 m	455 m	1·000	1·022	
570 s	580 s	580 s	585 s	0·983	0·991	
725 w	730 m	555 sh	555 sh	1·306	1·315	$\gamma(HOH)$
900 sh	900 sh	—	—	—	—	$\gamma(POH)$
1 005 s	1 010 s	745 m	750 m	1·349	1·347	$\delta(OPH)$
1 030 s	1 035 s	770 sh	765 w	1·338	1·353	
915 s	915 s	920 s	920 s	0·995	0·995	$\nu(PO)$
1 085 vs	1 080 vs	1 085 vs	1 085 vs	1·000	0·995	
1 120 vs	1 120 vs	1 120 vs	1 115 vs	1·000	0·996	
1 215 vs	1 215 vs	1 210 vs	1 220 vs	1·004	0·996	
—	—	855 w	860 w	—	—	$\delta(POD)$
1 660 w	1 650 w	—	—	—	—	$\delta(HOH)$
2 475 m	2 480 m	1 795 m	1 800 m	1·379	1·378	$\nu(PH)$
3 000 s	2 950 s	2 250 s	2 250 s	1·333	1·311	$\nu(OH)$ (POH)
3 450 sh	3 250 sh	2 450 sh	2 450 sh	1·408	1·383	$\nu(OH)$ (H_2O)

for the vibrations $\nu_{as}(PO)$, $\nu_s(OD)$, and $\nu_{as}(OD)$. The vibrations $\nu_s(PO)$, $\nu(PD)$, $\delta(DOD)$, and even $\delta(OPD)$ are not distinctly split up in the experimental arrangement applied. The analysis of the spectra in the $\delta(OPO)$ range is influenced unfavourably by the overlap with the region of the D_2O external vibrational bands and by the high

TABLE V

Raman Spectra of the Chromium(II) Phosphites Studied

Symbols used as in Table III.

$CrHPO_3 . H_2O$	$CrDPO_3 . 2 D_2O$	$CrH_4P_2O_6 . H_2O$	$CrD_4P_2O_6 . D_2O$	Assignment
140 s	—	100 m	100 sh	
—	—	135 vw	—	
—	—	185 vw	170 sh	
		280 w	280 w	
460 w	460 w	405 w	380 w	$\delta(OPO)$
590 w	600 w	460 vw	455 w	
	650 vw	540 vw	580 vw	
1 005 vs	1 000 s	895 w	890 w	$\nu(PO)$
1 065 w	1 065 w	1 080 vs	1 090 vs	
1 100 vw	1 100 sh	1 180 m	1 185 w	
—	—	1 255 vw	1 255 vw	
1 025 m	760 w	1 010 m	740 w	$\delta(OPH)$
1 035 m	—	1 030 m	760 w	
2 450 vs	1 770 m	2 470 vs	1 790 vs	$\nu(PH)$

TABLE VI

Factor Group Analysis of $CrDPO_3 . 2 D_2O$

T_A acoustic modes, T translatory lattice modes, R rotatory lattice modes, N_{int} number of internal vibrational modes, N_{tot} total number of vibrational modes

Type	N_{tot}	T_A	T	R	N_{int}	Activity
A	36	0	12	9	15	Ra
B_1	36	1	11	9	15	Ra, IR
B_2	36	1	11	9	15	Ra, IR
B_3	36	1	11	9	15	Ra, IR

background in the Raman spectrum. Unusual is the presence of six distinctly separated bands in the ν(OD) region (according to Table VII, two bands are anticipated in the site symmetry approach and twelve in the factor group approach); such clearly separated ν(OD) bands have not been observed in the spectra of any phosphite except the isostructural $CuDPO_3.2\,D_2O$ (ref.[23]). The low half band width of the ν(OD) bands is likely to be due to the coordination of the D_2O molecules to the Cr^{2+} (or Cu^{2+}) ions, sterically hindering the hydrogen bond formation between the D_2O molecules[3,12].

In the infrared spectrum of the phosphite $CrH_4P_2O_6.H_2O$, the δ(POH) and ν(PO) bands probably coincide at 1215 cm^{-1}. They can be distinguished not only on deuteration, but also on the study of the Raman spectra, where the ν(OH), δ(OH), and γ(OH) bands virtually do not appear at the gain used (*e.g.*[8] and Table V). The vibrational spectra of chromium(II) hydrogenphosphite indicate the presence of the so-called polyorthophosphite anion, *i.e.* an anion formed owing to the hydrogen bonding between the oxygen atoms and the hydroxyl groups bonded at two different phosphorus atoms[4–9,19,23]. In this respect the chromium(II) hydrogenphosphite differs from chromium(III) hydrogenphosphite, the latter being more precisely formulated as a complex phosphito-acid[24]. The hydrogen bond lengths in the phosphite $CrH_4P_2O_6.H_2O$ were determined based on the ν(OH) infrared absorption bands, employing five different correlation dependences[25–29], From the lengths obtained, the averages and probable deviations were calculated. In the polyorthophosphite anion the hydrogen bond length is 269 ± 2 pm; in addition, a weaker hydrogen bond, length 286 ± 2 pm, occurs in the crystal lattice of the substance, resulting probably from the interaction of the polyorthophosphite anion with the water molecule. In the hydrogen bond formation, the phosphite $CrH_4P_2O_6.H_2O$

TABLE VII

Correlation Table of the Internal Vibrations of the DPO_3^{2-} and D_2O Species

Vibration	Point group		Site symmetry		Factor group
DPO_3^{2-}	C_{3v}		C_1		D_2
δ_s(OPO), ν_s(PO), ν(PD)	$3A_1$	→	$3A$	→	$3(A + B_1 + B_2 + B_3)$
ν_{as}(PO), δ(OPD), δ_{as}(OPO)	$3E$	→	$6A$	→	$6(A + B_1 + B_2 + B_3)$
D_2O	Ca_{2v}		C_1		D_2
δ(DOD), ν_s(OD)	$2A_1$	→	$2A$	→	$4(A + B_1 + B_2 \mathrm{M} B_3)$
ν_{as}(OD)	B_1	→	A	→	$2(A + B_1 + B_2 + B_3)$

resembles the phosphite $CdH_4P_2O_6.H_2O$, where the X-ray diffraction patterns have revealed[30] a hydrogen bond within the polyorthophosphite anion, length 267 pm, and one between the anion and the water molecule, length 283 pm.

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