PHOSPHITES OF SOME TRIVALENT METALS FROM THE FIRST TRANSITION SERIES*

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Received October 27th, 1978

The phosphites $M_2(HPO_3)_3 \cdot 7\,H_2O$ ($M = V, Cr$), $MH_3P_2O_6.3\,H_2O$ ($M = V, Mn$) and $H_3[Cr(HPO_3)_3.10\,H_2O$ were studied in the solid phase by means of the thermography, magnetochemistry, and spectroscopy (IR, EPR, electronic reflection) techniques. The EPR spectrum of $V_2(HPO_3)_3.7\,H_2O$ at ambient temperature displays hyperfine splitting arising from the nucleus ^{51}V. In the phosphites $H_3[Cr(HPO_3)_3].10\,H_2O$, $MnH_3P_2O_6.3\,H_2O$, and probably also $VH_3P_2O_6.3\,H_2O$, in contrast to the other hitherto studied hydrogenphosphites, coordination of the HPO_3^{2-} anions occurs. These anions form with the molecules of the crystal water hydrogen bonds of the energy 40 kJ mol^{-1}. The Jörgensen's parameters of the ligand in the tris(phosphito)chromate(III) anion are $f = 0{\cdot}95$ and $h = 1{\cdot}50$.

The preparation and chemical analysis of the phosphites $V_2(HPO_3)_3.7\,H_2O$, $VH_3P_2O_6.3\,H_2O$, $MnH_3P_2O_6.3\,H_2O$, $Cr_2(HPO_3)_3.7\,H_2O$, and $H_3[Cr(HPO_3)_3]$. $.10\,H_2O$ have been described in the papers[1,2]. The optical activity of the phosphite $H_3[Cr(HPO_3)_3].10H_2O$ has evidenced the coordination of three bivalent phosphite anions[3,4]. The study of other physico-chemical properties of these compounds has been so far confined to a partial investigation of the solubility, density, and magnetic susceptibility[1,2]. In the present work, our study of trivalent metal phosphites[5,6] is continued with the aim to give a structure-bonding interpretation of the results obtained, particularly with regard to the nearest surrounding of the transition metal atom and the phosphite-transition metal interaction.

EXPERIMENTAL

Chemicals and Analytical Methods

The phosphites $M_2(HPO_3)_3.7\,H_2O$ ($M = V, Cr$) were prepared by reaction of vanadium(III) perchlorate[1] or chromium trichloride[2] with an equivalent amount of ammonium phosphite in aqueous solution. The phosphites $MH_3P_2O_6.3\,H_2O$ ($M = V, Mn$) and $H_3[Cr(HPO_3)_3]$. $.\,10\,H_2O$ were prepared by reaction of phosphorous acid with vanadium(III) acetate[1], dimanga-

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* Part XXVIII in the series Preparation and Properties of Phosphites; Part XXVII: This Journal *44*, 1353 (1979).

nese trioxide,[1] or chromium(III) phosphite[2]. The deuterated phosphites were prepared analogously employing D_3PO_3 as the starting substance. The isotope exchange in the OH groups (in contrast to the PH groups) in the vanadium(III) and manganese(III) phosphites was, however, incomplete; in deuterated chromium(III) phosphites the isotope contamination was negligible. The solutions of chromium trichloride and potassium phosphite in D_2O were prepared as described previously[6]. In view of the difficult crystallization, the phosphite $CrD_6P_3O_9.10\ D_2O$ was only prepared in solution.

The content of vanadium[7], manganese[1], and phosphorus[7-9] was determined cerimetrically, chromium was determined gravimetrically[2,6] as Cr_2O_3.

Physico-Chemical Measurements

The thermal decomposition was examined on an instrument Derivatograph (MOM, Budapest) with the temperature rise program 5 K min^{-1}; the vanadium(III) and manganese(III) phosphites were investigated in nitrogen atmosphere, the chromium(III) phosphites on air. The magnetic susceptibility was measured at ambient temperature by applying the Faraday method in the Terry's modification[10]. The EPR spectra were run at ambient temperature on an instrument Varian E4 in the range of 3 cm, the electronic reflection spectra on a spectrophotometer VSU-2 (Zeiss, Jena). The parameters Dq and B for the vanadium(III) phosphites were calculated according to Boxall and coworkers[11]; for the chromium(III) phosphites this procedure failed, the parameters were therefore determined graphically.

The infrared absorption spectra were scanned on a spectrophotometer UR 20 (Zeiss, Jena) by using the KBr disk and nujol and tripene mull techniques.

All operations with the vanadium(III) phosphites were performed in nitrogen inert atmosphere.

RESULTS AND DISCUSSION

During the thermal decomposition, the phosphite $V_2(HPO_3)_3.7\ H_2O$ liberates in the region of 310 – 500 K gradually 6·2 molecules of water; the corresponding endo-effect has a minimum at 365 K.The phosphite $VH_3P_2O_6.3\ H_2O$ exhibits two endo-effects with the minima at 360 and 430 K pertaining to the dehydration; the weight decrease in the range 320 – 650 K proceeds, however, smoothly, and corresponds to the total of 2·2 molecules of water. In the case of the phosphite $MnH_3P_2O_6.3\ H_2O$, the primary process is exothermic decomposition into compounds involving bivalent manganese (beginning at 385 K). The exothermic decomposition of the phosphite anion in the phosphite $V_2(HPO_3)_3.7\ H_2O$ begins at 530 K, in the phosphite $VH_3P_2O_6.3\ H_2O$ at 570 K. The chromium(III) phosphite $Cr_2(HPO_3)_3.7\ H_2O$ evolves in the range 340 – 600 K gradually 6·7 molecules of water; the corresponding endo-effect has the minimum at 390 K. Similarly behaves also $H_3[Cr(HPO_3)_3].10\ H_2O$, evolving in the range of 340 – 520 K 10 molecules of water with the endo-effect minimum at 380 K. A survey of the other properties studied is given in Table I.

The magnetic moments of the substances are close to the "purely spin values", which corresponds to zero orbital contribution from the ^5E_g and $^4A_{2g}$ states or its compensation in the $^3T_{1g}$ state by the competitive effects of distortion of the coordination sphere, spin-orbital interaction, and electron delocalization.

TABLE I

Parameters of the Phosphites Studied at Ambient Temperature

Quantity	$H_3[Cr(HPO_3)_3].10H_2O$	$M_2(HPO_3)_3.7H_2O$		$MH_3P_2O_6.3H_2O$	
		M = Cr	M = V	M = V	M = Mn
	Magnetic measurements				
μ_{eff} (B. M.)	3·85	3·91	2·75	2·89	4·90
	Electron paramagnetic resonance				
g	1·981	1·975	1·997	no signal	2·013
HFS, kA/m	—	—	9·154	—	—
	Electronic reflection spectroscopy				
σ_1, μm^{-1}	1·59	1·64	1·45	1·54	1·30
σ_2, μm^{-1}	2·22	2·22	2·19	2·22	1·96
σ_3, μm^{-1}	3·45	—	3·09	2·99	—
$10Dq$, μm^{-1}	1·59	1·64	1·59	1·46	1·96
B, mm^{-1}	63	71	58	51	—
	Infrared absorption spectroscopy[a]				
δ(OPO)					425 sh
	440 m				460 m
	480 sh	540 sh			480 sh
					570 sh
	580 m	590 s	605 m	590 m	620 s
	760 sh				
δ(OPH)	1 005 sh	1 050 sh	1 040 sh	1 020 sh	1 025 vs
δ(OPD)	750 s	775 m	760 m	750 m	760 m
ν(PO)	940 m	950 sh	1 010 sh	955 sh	985 s
	1 050 sh		1 085 sh	1 080 vs	1 065 vs
	1 090 s	1 100 vs	1 150 vs	1 210 vs	1 100 vs
	1 145 sh				
	1 210 sh				
ν(OH) (H_2O)	1 650 m	1 635 m	1 645 m	1 640 m	1 645 m
ν(PH)	2 460 m	2 435 m	2 430 m	2 445 m	2 500 w
					2 520 w
ν(PD)	1 790 m	1 765 w	1 760 m	1 790 m	1 815 w
					1 825 w
ν(OH) (H_2O)	3 000 sh	3 000 sh	3 000 sh	3 000 sh	
	3 450 vs	3 440 vs	3 400 vs	3 430 vs	3 430 vs
2δ(OH) (H_2O)	3 300 sh	3 250 sh	3 200 sh	—	3 250 sh

[a] Band positions in cm^{-1}; assignment: ν stretching vibrations, δ bending vibrations; relative band intensity: vs very strong, s strong, m medium, w weak, sh shoulder.

The EPR spectrum of the phosphite $VH_3P_2O_6.3\,H_2O$ agrees with the currently observed behaviour of vanadium(III) compounds with two unpaired electrons[12-14]. In contrast with this is the spectrum of $V_2(HPO_3)_3.7\,H_2O$, comprising eight separate bands resulting from the hyperfine splitting by the nucleus ^{51}V ($I_N = 7/2$). It is conceivable that this rather rare phenomenon appears owing to the increase of the relaxation time due to the splitting by the ligand field and distortion of the latter.

The bands $\sigma_1 - \sigma_3$ in the electronic reflection spectra of the vanadium(III) and chromium(III) phosphites arise from the three spin-allowed *intra*-configuration transitions. Noticeable is the relatively high intensity of the two-electron transition band σ_3 of the vanadium(III) phosphites, probably accounted for by the interaction with the charge transfer band and possibly also a vibronic or configuration interaction[15]. The chromium(III) phosphites, too, exhibit an overlap of the σ_3 band with the charge transfer band. The σ_2 band of the phosphite $MnH_3P_2O_6.3\,H_2O$ belongs obviously to the $^5T_{2g} \rightarrow {}^5E_g$ transition. The interpretation of the comparatively weak σ_1 band is uncertain; it has been suggested that it may be due to the *CT* transition. forbidden according to Lapporte[16].

Based on the spectrum of the phosphite $H_3[Cr(HPO_3)_3.10\,H_2O$ the Jörgensen's parameters for the coordinated phosphite anion were determined to be $f_{HPO_3} = 0{\cdot}95$ and $h_{HPO_3} = 1{\cdot}50$. These values are in accordance with the conclusions from our previous study of nickel(II) (ref.[17]), cobalt(II) (ref.[17]), iron(II) (ref.[18]) and chromium(II) (ref.[19]) phosphites.

The infrared absorption spectrum of the phosphite $MnH_3P_2O_6.3\,H_2O$ does not display the P—O—H stretching or bending vibrations, observed, *e.g.*, for the homologous phosphite[5] $FeH_3P_2O_6.3\,H_2O$ (Fig. 1) and many other transition metal hydrogenphosphites[18-20]. Taking into account the results of the optical activity investigations[3,4], the band at 1210 cm^{-1} of the phosphite $H_3[Cr(HPO_3)_3].10\,H_2O$ is to be attributed to the PO stretching rather than the POH bending vibration, which also occurs in this wavenumber range[5,18-20]. The band at 1210 cm^{-1} appears also in the spectrum of the phosphite $VH_3P_2O_6.3\,H_2O$. In this case there are no other structure data available, thus we attribute it also to the ν(PO) vibration only based on the overall analogy of the vibrational spectra of the phosphites $H_3[Cr(HPO_3)_3].10\,H_2O$ and $MH_3P_2O_6.3\,H_2O$ (M = Mn, V) (see Fig. 1). These spectra are seen to differ on the whole from the spectrum of iron(III) dihydrogenbis(orthophosphite) containing P—O—H groups[5]. Use cannot be made of deuteration for a more reliable assignment of the band at 1210 cm^{-1}, since with the low spectral resolution a coincidence of the δ(ODO) and ν_{as}(PO) bands and also of the δ(POD) and ν_s(PO) bands is very likely (we denote as ν_s(PO) and ν_{as}(PO) the lowest and highest frequency bands, respectively, of the ν(PO) grouping). From the suggested assignment of the band at 1210 cm^{-1} it follows in turn that the band at 3000 cm^{-1} is not associated with the vibration of the POH group, but with the stretching vibration of the HOH group in the hydrogen bond "water–anion", as in the case of double alkali-chromium(III) phosphites[6], where the presence of the POH groups is ruled out. The energy of the hydrogen bonds "water–anion" determined according to Yukhnevich and Karyakin amounts to 40 kJ mol^{-1}, which is in agreement with the conclusion[21] on the positive hydration of the HPO_3^{2-} anion. An almost the same value of the "water–anion" hydrogen bond energy is obtained for the phosphites $M_2(HPO_3)_3.7\,H_2O$ (M = V, Cr); for the homologous compound $FeH_3P_2O_6.3\,H_2O$, however, an appreciably lower value (30 kJ mol^{-1}) has been established[5]. This comparison also points to the coordination of the HPO_3^{2-} anion to the central atom in the phosphite $VH_3P_2O_6.3\,H_2O$.

The ν(POH) and δ(POH) bands being absent and the spectrum comprising few rather broad bands, the spectra of all the phosphites studied resemble those of substances involving the HPO_3^{2-} anions (see [5,18–20]) rather than those of substances with hydrogen bond POH···OP in the so-called polyorthophosphite anion[5,18–20,22].

From the previous spectroscopical[17–20,22,23] and X-ray diffraction[24,25] studied it follows that the formation of polyorthophosphites is peculiar to hydrogenphosphites of bivalent metals and, of trivalent metals, only of Fe^{3+}. In the vanadium(III), chromium(III), and manganese(III) phosphites a tendency is obvious to a weakening of the effect of the hydrogen bond due to the competitive influence of the coordination covalent bond, the phosphito-complex being best defined for the phosphite $H_3[Cr(HPO_3)_3].10\,H_2O$, which also possesses the highest stabilization energy of the crystal field. Also from a comparison of the compounds $MH_3P_2O_6.3\,H_2O$ in the series M = Fe (ref.[5]), Mn, V emerges a possible effect of the crystal field stabilization energy, as the defined polyorthophosphite is here created only if this energy is zero.

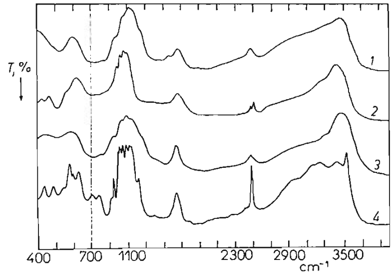

FIG. 1

Infrared Absorption Spectra of the Phosphites Studied

1 $VH_3P_2O_6.3\,H_2O$, *2* $MnH_3P_2O_6.3\,H_2O$, *3* $H_3[Cr(HPO_3)_3].10\,H_2O$, *4* $FeH_3P_2O_6.3\,H_2O$.

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Translated by P. Adámek.