

Preparation and Properties of Hydrogen Tris(monohydrogen phosphito) Ferrate(III) and Hydrogen Tris(monohydrogen phosphito) Chromate(III)

RAJINDER N. PURI* and R. OWEN ASPLUND

Department of Chemistry and Division of Biochemistry, The University of Wyoming, Laramie, Wyo. 82071, U.S.A.

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The preparation, and, spectral and magnetic properties of hydrogen tris(monohydrogen phosphito) ferrate(III) and hydrogen tris(monohydrogen phosphito) chromate(III) are described. Infrared spectral properties of the complexes show the presence of considerable dissymmetry in these complexes. The magnetic moment of the complexes, at 294 K, have been found to be anomalously high.

Introduction

An earlier report by these authors [1] described the preparation and spectral, and magnetic properties of trinuclear oxobridged iron(III)–L-amino acid tris(dihydrogen phosphito) nitrates which have been considered as possible models for the ferritin iron core. During the course of an investigation [2] of the infrared spectral properties of the above complexes, containing the nucleus $[\text{Fe}_3\text{O}]^{7+}$, it was decided to explore the infrared spectral characteristics of complexes containing only iron(III) and phosphorus containing ligands since there is a paucity of information on such complexes. We were particularly interested in the examination of infrared spectral properties of iron–oxygen stretching modes and various phosphorus–oxygen stretching modes in complexes containing iron(III) and unsubstituted phosphorus containing ligands. One report [3] describes the preparation and electromeric properties of hydrogen tris(monohydrogen phosphito) chromate(III) complex [Fig. 1a], also known as triphosphitochromic acid [4]. However, its spectral and magnetic properties remained uninvestigated. It appeared to us that an investigation of the spectral and magnetic properties of the anionic complex derived from chromium(III) along with parallel studies on similarly constituted anionic complex

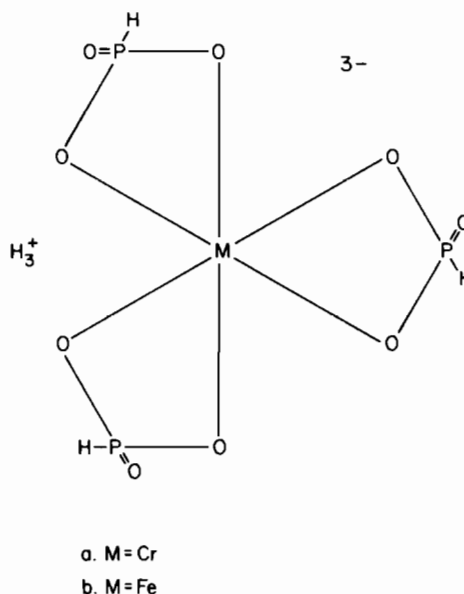


Fig. 1. Schematic representation of the molecular structure of: (a) Hydrogen tris(monohydrogen phosphito) chromate(III), (b) Hydrogen tris(monohydrogen phosphito) ferrate(III).

derived from iron(III) [Fig. 1b] would be well suited for our needs. This paper describes the preparation and spectral, and magnetic properties of hydrogen tris(monohydrogen phosphito) chromate(III) and hydrogen tris(monohydrogen phosphito) ferrate(III). One of the most unusual features of these complexes is their high magnetic moments at 294 K.

Experimental

Preparation of the Complexes

Hydrogen tris(monohydrogen phosphito) ferrate(III). The complex was prepared from either ferric nitrate (Method A) or ferric chloride (Method B), as follows: ferric nitrate nonahydrate (4.104 g) or ferric chloride hexahydrate (2.700 g) was mixed

*Author to whom correspondence should be addressed. Present address: Department of Physiological Chemistry, University of Wisconsin Medical Center, 1215 Linden Drive, 589 Medical Sciences Building, Madison, Wis. 53706, U.S.A.

with phosphorous acid (3.270 g) and urea (0.600 g) in 350 ml water (molar ratios 2:1:2). The reactants were stirred under reflux at 90 °C for three days. During the course of reaction, a thick white precipitate separated. Following reflux, the reaction mixture was cooled to room temperature and filtered. The precipitate was washed with water and then with ethanol (95%) and air dried overnight. Yield; ferric nitrate (Method A) 2.005 g (67%), ferric chloride (Method B) 2.063 g (69%).

Hydrogen tris(monohydrogen phosphito) ferrate(III) (Method C). Ferric nitrate nonahydrate (4.104 g) was dissolved in 50 ml water. Ferric hydroxide was precipitated by the addition of ammonium hydroxide solution to the ferric nitrate solution until the pH of the reaction mixture was *ca.* 8. The solution containing the freshly precipitated iron(III) hydroxide was added to a boiling solution of phosphorous acid (3.690 g in 150 ml water). The reaction mixture was refluxed gently for 2 h; it was then cooled to room temperature and the white precipitate so formed was filtered, washed with water and then with ethanol (95%), and air dried overnight to yield the complex (2.147 g, 72%).

Hydrogen tris(monohydrogen phosphito) chromate(III). The complex was prepared by the method of Podlaha and Ebert [3]. Chromium nitrate nonahydrate (4.002 g) was dissolved in 50 ml water. Chromium hydroxide was precipitated at pH 8 by the addition of ammonium hydroxide. The solution containing the freshly precipitated chromium(III) hydroxide was added to a boiling solution of phosphorous acid (4.905 g in 150 ml water). The reaction mixture was refluxed gently for 2 h. It was then cooled to room temperature and allowed to evaporate at room temperature to dryness. The gummy mass so obtained was macerated with ethanol (absolute) and stirred in ethanol (absolute) for 4 h at room temperature. The green precipitate so formed was filtered, washed with ethanol (absolute), and air dried overnight to yield the complex (3.600 g, 89%).

Elemental Analysis

Metal analyses were performed by Huffman Laboratories, Inc. and the Chemical and Bacteriological Laboratory of the Wyoming Department of Agriculture.

Electronic Spectra

Solid state electronic spectra of the complexes, in the visible and near infrared regions, were obtained on Cary 14R Spectrophotometer in nujol; nujol mulls were mounted between the quartz plates.

Infrared Spectra

Infrared spectra were obtained on an automatic recording, double-beam-optical null IR 10 Infrared

Spectrophotometer from Beckman Instruments. The spectra were recorded using KBr pellets.

Magnetic Measurements

Magnetic susceptibility measurements at, 294 K, on solid samples were made on a Faraday balance consisting of Cahn DTL Electrobalance. The Faraday balance was calibrated with $\text{CoHg}(\text{CNS})_4$. Molecular weights needed to calculate molar magnetic susceptibilities were estimated from analytical data.

Results and Discussion

Analyses of iron and chromium in the complexes hydrogen tris(monohydrogen phosphito) ferrate(III) [Found: Fe, 18.67%; $\text{H}_3[\text{Fe}(\text{HPO}_3)_3] \cdot \text{H}_2\text{O}$ requires Fe, 18.12%] and hydrogen tris(monohydrogen phosphito) chromate(III) [Found: Cr, 13.01%; $\text{H}_3[\text{Cr}(\text{HOP}_3)_3] \cdot 6\text{H}_2\text{O}$ requires Cr, 12.90%] were found to be satisfactory for the given chemical postulations. It has been our experience that repeated attempts to achieve correct analytical results for phosphorus content of the complexes described in this work were unsuccessful. We have encountered similar difficulties with trinuclear oxo-bridged iron(III)-L-amino acid tris(dihydrogen phosphito) nitrates [1] and iron(III) tris(monohydrogen phosphito) chloride [5] described elsewhere. Podlaha *et al.* [4] made similar observations during their investigations of triphosphito chromic acid. This observation also suggests that phosphorous acid is not present as a monodentate ligand but is ligated to the metal ions in a bidentate fashion.

The solid state electronic spectrum of hydrogen tris(monohydrogen phosphito) chromate(III) [Fig. 1a], show three prominent bands (Table I): band I, 22,988 cm^{-1} , band II, 16,666 cm^{-1} , and band III, 14,925 cm^{-1} . The electronic spectra of some of the compounds containing chromium(III) in the high spin d^3 configuration are also presented in Table I for comparison. Hush and Hobb [6] have discussed the electronic spectra of the high spin d^3 chromium compounds in detail: the two bands corresponding to transitions ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ dominate the spectra of chromium(III) complexes and occur at *ca.* 17,500 and *ca.* 24,000 cm^{-1} respectively. These transitions are spin allowed and show large molar extinction coefficients. Lever *et al.* [7] in their study of the chromium complex of picolinic acid N-oxide, $\text{Cr}(\text{picO})_3 \cdot \text{H}_2\text{O}$, have attributed the electronic spectral bands at 17,550 and 24,400 cm^{-1} to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ transitions respectively. The chromium complex in this work exhibits absorption bands at 16,666 cm^{-1} (band II) and 22,988 cm^{-1} (band I) which may be attributed to the transitions ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ respectively. The third band in the spectra of known chromium(III) com-

TABLE I. Electronic Spectral Bands of Hydrogen Tris (monohydrogen phosphito) Chromate(III) and Compounds Containing Chromium(III) in the Solid State.

Compound	Band Assignment, ν_{\max} (cm ⁻¹)		
	Band I	Band II	Band III
H ₃ [Cr(HPO ₃) ₃]·6H ₂ O ^a (in nujol)	22,988	16,666	14,925
Cr ₂ O ₃ ^b	23,000	16,800	
Cr ₂ O ₃ (MgO) ^b	22,700	16,200	
Cr ³⁺ in corundum	24,400, 25,000	18,000, 18,450	14,957
Cr ³⁺ in NaMgAl(C ₂ O ₄) ₃ ·9H ₂ O ^b	23,670	17,316, 17,620	14,476, 15,287
Cr(picO) ₃ ·H ₂ O ^c	24,400	17,550	

^aThe spectra in aqueous solution showed absorption bands at 14,705, 15,385, 15,873, and 22,727 cm⁻¹. ^bReference 6. ^cReference 7, picO = picolinic acid N-oxide.

plexes [6] occur in the range 14,000–15,000 cm⁻¹ and is attributed to the transition ${}^4A_{2g} \rightarrow {}^2E_g$ or/and ${}^2T_{1g}$ (2F): the spectrum of hydrogen tris(monohydrogen phosphito) chromate(III) exhibits a band at 14,295 cm⁻¹ which probably corresponds to the transition ${}^4A_2 \rightarrow {}^2T_1$ [6]. It should be mentioned here that under the experimental conditions employed to investigate the spectra of the chromium(III) chelate in this work, it was not possible to measure the molar extinction coefficient. The electronic spectrum of the chromium(III) complex described is consistent with the fact that chelate in question contains high spin d³ chromium in cubic ligand field. Puri *et al.* have investigated the spectra of iron(III)–L-amino acid complexes containing the trinuclear oxo-bridged iron(III), [Fe₃O]⁷⁺, unit [1, 8] and dinuclear dialkoxo-bridged iron(III), [Fe₂(OR)₂]⁴⁺, unit [9]. The electronic spectra of complexes containing the trimeric iron(III) unit, [Fe₃O]⁷⁺, show bands at *ca.* 11,000 and *ca.* 21,000 cm⁻¹ while the ones containing the dinuclear dioxo-bridged unit, [Fe₂(OR)₂]⁴⁺, show absorption bands at *ca.* 11,000 and *ca.* 16,000 cm⁻¹. The lower energy band in the spectra of complexes containing either [Fe₃O]⁷⁺ unit or [Fe₂(OR)₂]⁴⁺ unit is attributed to ${}^6A_1 \rightarrow {}^4T_1$ transition and the higher energy band to ${}^6A_1 \rightarrow {}^4T_2$ transition. The electronic spectrum of the hydrogen tris(monohydrogen phosphito) ferrate(III) shows two bands (Table II): band I, 10,204 cm⁻¹ and band II 13,517 cm⁻¹. It is clear, thus, that the iron(III) complex in this work does not contain either [Fe₃O]⁷⁺ unit or [Fe₂(OR)₂]⁴⁺ unit because the higher energy transition ${}^6A_1 \rightarrow {}^4T_2$ in its electronic spectrum lies at 13,517 cm⁻¹. However, the electronic spectra of known unbridged iron(III) complexes [10] show absorption bands [Table II] at *ca.* 10,000 cm⁻¹ and *ca.* 13,000 cm⁻¹ and have been assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ transitions

TABLE II. Electronic Spectral Bands of Hydrogen Tris (monohydrogen phosphito) Ferrate(III) and Complexes not Containing Any Fe(III)–O–Fe(III) Bridge.

Complex	Solvent	Band Assignment, ν_{\max} (cm ⁻¹)	
		Band I	Band II
H ₃ [Fe(HPO ₃) ₃]·XH ₂ O	Nujol	10,204 ^b	13,157 ^b
[Fe(acac) ₃] ^a	Cyclohexane	9,760	13,200
[Fe(DPM) ₃] ^a	Acetone	9,900	13,160

^aReference 10. acac = acetylacetonate, DPM = 2,2,6,6-tetramethyl heptane-3,5-dione. ^bSame for the complex obtained by methods of preparation A, B, and C.

respectively. Since the electronic spectrum of the iron(III) chelate in this work resembles those of the known iron(III) complexes containing the unbridged structural unit, [Fe(III)O₆]_{oct}, their molecular structures should also be very similar [Fig. 1b]. It is interesting to note that absorption bands due to the transition ${}^6A_1 \rightarrow {}^4T_2$ in the spectra of trinuclear oxo-bridged iron(III) complexes, dinuclear dioxo-bridged iron(III) complexes, and unbridged iron(III) complexes are found at *ca.* 21,000, 16,000, and 13,000 cm⁻¹ respectively and can be used to distinguish among these [9]. The two transitions in the electronic spectra of the iron(III) complexes discussed are spin forbidden and consequently should exhibit very low extinction coefficient; however, this could not be verified in the present case because of the nature of experimental conditions used to record the electronic spectrum.

The infrared spectra of chromium(III) and iron(III) chelates in this study [Tables III and IV] show extensive similarities. Both chelates show

TABLE III. Infrared Spectral^a Data of Hydrogen Tris(monohydrogen phosphito) Chromate(III) and Hydrogen Tris(monohydrogen phosphito) Ferrate(III).

Complex	Spectral Frequency Assignment (cm ⁻¹)		
	$\nu(\text{PH})$	$\nu(\text{P=O})$	$\nu(\text{M-O})$
H ₃ [Cr(HPO ₃) ₃]·6H ₂ O	2420 b,w 2440 b,w 2460 sh,w	1220 sh,m 1140 b,s 1070 b,s	590 b,w, 530 sh,w, 480 sh,w, 430 b,w, 330 b,w
H ₃ [Fe(HPO ₃) ₃]·xH ₂ O	2400 shp,m ^b 2430 shp,s 2460 shp,w	1200 sh,m ^b 1160 sh,s 1140 b,s	600 shp,m ^b 570 sh,w, 510 shp,w, 460 sh,w, 430 shp,w, 380 sh,w, 330 shp,m

^aAbbreviations: b, broad; shp, sharp; sh, shoulder; w, weak, m, medium; s, strong. ^bSame for the complex obtained by methods of preparation A, B, and C.

TABLE IV. Infrared Spectral^a Data of Hydrogen Tris(monohydrogen phosphito) Chromate(III) and Hydrogen Tris(monohydrogen phosphito) Ferrate(III).

Complex	Spectral Frequency Assignment (cm ⁻¹)	
	$\nu_{\text{asym}}(\text{H}_2\text{O})$ and $\nu_{\text{sym}}(\text{H}_2\text{O})$	H ₂ O of crystallization
H ₃ [Cr(HPO ₃) ₃]·6H ₂ O	3500 shp,s 3400 b,s	1650 b,w, 1640 sh,w
H ₃ [Fe(HPO ₃) ₃]·xH ₂ O	3480 b,s ^b 3200 b,s	1650 b,w ^b

^aAbbreviations: b, broad; w, weak; shp, sharp; sh, shoulder; asym, asymmetric; sym, symmetric. ^bSame for the complex obtained by methods of preparation A, B, and C.

absorption bands at *ca.* 2420 cm⁻¹ (Table III) corresponding to P–H stretching mode [11, 12]. The presence of bands in the region 1220–1050 cm⁻¹ (Table III) correspond to the presence of three hydrogen bonded phosphoryl, P=O, groups [11, 12] in these complexes. The high resolution of the bands in the infrared spectra of the complexes, in this work, in the regions corresponding to P–H and P=O stretches signifies the fact that there is considerable dissymmetry present in their structures. Furthermore, phosphorous acid, in the complexes in this work, acts as a bidentate ligand by co-ordinating to the central metal ion through the two hydroxyl functions so as to transfer two units of negative charge to the central metal ion thus leaving the

P=O and P–H functions intact to be seen in the infrared spectrum. This is in agreement with our investigation on the infrared spectral properties of iron(III) tris(monohydrogen phosphito) chloride [5] which contains phosphorous acid ligated to iron(III) in a manner analogous to the one in complexes in this work. Alternatively, phosphorous acid can ligate to iron(III) through P=O and P–OH groups in a manner similar to the ligation of L-amino acids through their carboxyl function to iron(III) in iron(III)–L-amino acid tris(dihydrogen phosphito) nitrates described elsewhere [1]. However, based on the infrared spectral evidence presented here the later mode of ligation of phosphorous acid to iron(III) in complexes in this work can be ruled out. The infrared spectra of the complexes in this work also exhibit bands in the low energy regions 600–550 cm⁻¹, 450–430 cm⁻¹, and 380–330 cm⁻¹ (Table III). These bands are characteristic of metal–oxygen (M–O) bonds present in these complexes. Griffith [13] and Long *et al.* [14] have suggested that asymmetric Fe–O stretch should occur in the region 600–500 cm⁻¹. Hancock and Thronton [15] have stressed that in the trivalent metal series, metal–oxygen stretching mode, ν_{11} , follows the same trend as the crystal field stabilization energies (CFSE) of the metals. The Fe–O stretching mode in K₃[Fe(OX)₃]·3H₂O has been assigned to absorption bands at 528 and 366 cm⁻¹ in the infrared spectrum of the complex [16]. Mikami *et al.* [17] performed normal coordinate analysis on the 1:3 (octahedral) models of various acetylacetonate complexes and assigned bands at 664, 559, 443, and 298 cm⁻¹ to the Fe–O stretch in the complex Fe(acac)₃.

TABLE V. Magnetic Susceptibility and Magnetic Moment Data of Hydrogen Tris(monohydrogen phosphito) Chromate(III) and Hydrogen Tris(monohydrogen phosphito) Ferrate(III).

Complex	Temperature (K)	$\chi_M \times 10^6$ (cgsu)	μ_{eff} (BM)
$\text{H}_3[\text{Cr}(\text{HPO}_3)_3] \cdot 6\text{H}_2\text{O}$	294	10,256	4.93
$\text{H}_3[\text{Fe}(\text{HPO}_3)_3] \cdot x\text{H}_2\text{O}$	294	24,021 ^a	7.54 ^a

^aSame for the complex obtained by methods of preparation A, B, and C.

Nakamoto *et al.* [18] have shown that the band at 300 cm^{-1} in the spectrum of $\text{Fe}(\text{acac})_3$ displayed maximum shift upon isotopic substitution and was accordingly assigned the Fe–O stretch; smaller shifts were observed for the bands appearing at 436, 511, 562 and 655 cm^{-1} . Tucker *et al.* [19] assigned the band at 570 cm^{-1} to Fe–O asymmetric stretch in the infrared spectra of iron(III)–L-amino acid perchlorates. Based on the preceding discussion it is not possible for us to qualify the observed spectral frequencies in the region $600\text{--}300 \text{ m}^{-1}$ in the infrared spectra of hydrogen tris(monohydrogen phosphito) ferrate(III) with respect to either asymmetric or symmetric Fe–O stretching mode but they are simply assigned to Fe–O stretching mode. Further qualification with regard to specific assignments must await appropriate isotopic substitution. The infrared spectra of $^{50}\text{Cr}(\text{acac})_3$ and $^{53}\text{Cr}(\text{acac})_3$ has been discussed by Nakamoto [20]. It is to be noted that bands at 463.4 and 358.4 cm^{-1} in the spectrum of the $^{50}\text{Cr}(\text{acac})_3$ exhibit negative shifts of 3.0 and 3.9 cm^{-1} respectively, where other bands exhibit negligible shifts by ^{50}Cr and ^{53}Cr substitution. Similar absorption bands have been observed in the spectrum of hydrogen tris(monohydrogen phosphito) chromate(III) (Table III). In a study of metal tropolonate complexes of chromium and iron carried out by Hulett and Thornton [21], the band at *ca.* 370 cm^{-1} has been attributed to M–O stretching mode. These workers also assigned the $\nu(\text{M–O})$ of trivalent metal tropolonates to absorption in the region $660\text{--}580 \text{ cm}^{-1}$, based on $^{16}\text{O}\text{--}^{18}\text{O}$ isotope shifts observed for the Cu(II) complex by Hutchinson *et al.* [22]. The infrared spectrum of the chromium(III) chelate in this work contains several bands in the region $600\text{--}300 \text{ cm}^{-1}$. They are simply assigned to Cr–O stretching modes. The broad absorption band at *ca.* 1650 cm^{-1} in the spectrum of the two chelates in question (Table IV) has been assigned to water of crystallization [23] and HOH bending modes [20, 23, 24]. The infrared spectrum of the iron(III) and chromium(III) chelates in this work also show broad and strong absorption band at *ca.* 3500 cm^{-1} (Table III) and is attributable to asymmetric and symmetric O–H stretching modes [20, 23, 24].

The molar magnetic susceptibility of the chromium(III) and iron(III) chelates at 294 K was found to be $10,256 \times 10^6$ and $24,021 \times 10^6$ cgsu respectively, the corresponding magnetic moment values were estimated to be 4.93 and 7.54 BM (Table V). The values of the magnetic moment of high spin d^3 chromium and high spin d^5 iron complexes, containing unbridged metal ions, can be calculated from the spin only magnetic moment relationship discussed elsewhere [25]. The values of the magnetic moment for chromium(III) and iron(III) chelates in this study are far too high for spin only magnetic moment of these complexes; they correspond to a value of 2.52 and 2.54 for the Lande's factor, *g*. This is very suggestive of orbital contribution to the total magnetic moment of these complexes. Experimentally the values of *g* are known to vary from 1.8 to 2.5 [26]. The value of *g* is inversely proportional to Δ , the magnitude of the ligand field splitting and directly proportional to Δ_e , the spin–orbit coupling constant for a given transition metal ion [25–27]. The anomalous magnetic behaviour of these two complexes awaits further investigation of the chelates by ESR method to verify the effect of spin–orbit coupling contribution to the high *g* values indicated by their large magnetic moments.

The chromium(III) and iron(III) chelates described in this paper provide important and direct information concerning the metal–oxygen and phosphorus–oxygen stretch frequencies because of the presence of unsubstituted phosphorus containing ligands in their structures. The abnormally high magnetic moment of the chelates surely provide an interesting puzzle for further investigation.

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