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Preparation and Properties of Tri-μ_3-Oxo-Triaquotris(L-Amino Acid) Tris(Dihydrogen Phosphito)triiron(III) Nitrates: Synthetic Probes for the Ferritin Iron Core

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Among all the models proposed for the structure of the ferritin iron core, iron(III)-L-amino acid perchlorates and nitrates containing the $[Fe_3O]^{7+}$ unit are among the most attractive because of the similarity between their physical properties and those of the ferritin iron core. The role of phosphorus in the structural organization of the ferritin iron core is less well understood. The tri-μ_3-oxo-triaquotris(L-amino acid)-tris(dihydrogen phosphito)triiron(III) nitrates, with the general formula, $[Fe_3O(L\text{-amino acid})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$, containing the unit $([Fe_3O]^{7+}$, have been prepared from a variety of L-amino acids and their spectral and magnetic properties investigated. They are much like those of the known complexes having the $[Fe_3O]^{7+}$ unit. It is therefore concluded that the iron(III) complexes containing the $[Fe_3O]^{7+}$ unit remain promising candidates as synthetic models of the ferritin iron core. The presence of the phosphorus containing ligand has minimal effect on the spectral and magnetic properties of iron(III) L-amino acid complexes containing the $[Fe_3O]^{7+}$ unit – an observation made with regard to the ferritin iron core some time ago.

Introduction

The role of phosphate in the ferritin iron core containing ferric hydroxy phosphate [1] is unclear. The iron core of ferritin, freed of phosphate, has been found to give the same diffraction patterns [2] as intact ferritin. Chrichton [3] has pointed out that phosphate does not seem to contribute significantly to the diffraction pattern, nor does it appear to be an essential component of the core. Confirmation of this view is provided by the observation that ferritins reconstituted from apoferritin and synthetic iron polymers [1, 4] devoid of any phosphorus show the same physical properties [1, 5, 6] *e.g.*, electron microscopy, sedimentation velocity behaviour, X-ray diffraction pattern, and electrophoretic mobility as the native ferritin; whether or not they retain biological activity is unknown. Van Kreel *et al.* [7], based on their studies on the incorporation of ^{59}Fe, [^{3}H]-leucine, and [^{33}P]-inorganic phosphate, have concluded that ferritin phosphate is in a dynamic state of equilibrium with inorganic phosphate of liver and serum. Harrison *et al.* [8] have suggested that there might be relationship between molecular stability of the native protein and negatively charged phosphate groups in the core of the protein. In the light of available information, the role of phosphorus in the structural organization of the ferritin iron core has remained uncertain. It was therefore decided to make synthetic models containing iron, phosphorus, and L-amino acids and to examine the spectral and magnetic properties of these complexes. A comparison of these properties with those of the trinuclear oxobridged iron(III)-L-amino acid perchlorates [9, 10] (Fig. 1a) and nitrates [11] (Fig. 1b) proposed as models for the ferritin iron core, might increase the understanding of the role of phosphorus in the structural organization of the ferritin iron core. It was necessary that a strategy aimed at incorporating phosphorus-containing ligands into the trinuclear oxobridged iron(III) nucleus be devised if necessary. It was found that a mixture in water of an L-amino acid, ferric nitrate nonahydrate, and phosphorous acid, in the molar ratio 2:1:0.5 stirred at 90°, led to the incorporation of phosphorous acid ligand into trimeric unit $[Fe_3O]^{7+}$. The choice of ferric nitrate and not ferric perchlorate or ferric chloride as the iron(III) reagent has been discussed elsewhere [12] in detail. This paper describes the preparation and properties of the novel complexes, tri-μ_3-oxo-triaquotris(L-amino acid)tris(dihydrogen phosphito)triiron(III) nitrates (Fig. 2) derived from eight L-amino

#Paper No. 8 in a Series. See References for preceding papers.

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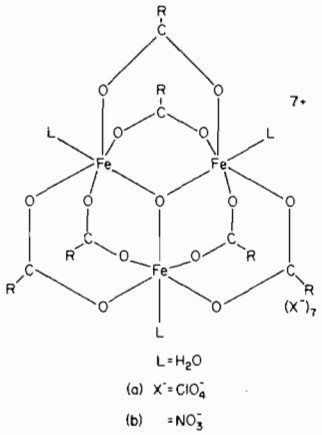

Fig. 1. The molecular structure of trinuclear oxobridge iron(III) L-amino acid complexes. (a) $[Fe_3O(L\text{-amino acid})_6(H_2O)_3](ClO_4)_7$. Structure established by X-ray crystal analysis and by spectral and magnetic properties [9, 10, 28]. (b) $[Fe_3O(L\text{-amino acid})_6(H_2O)_3](NO_3)_7$. Structure established by spectral and magnetic properties [11].

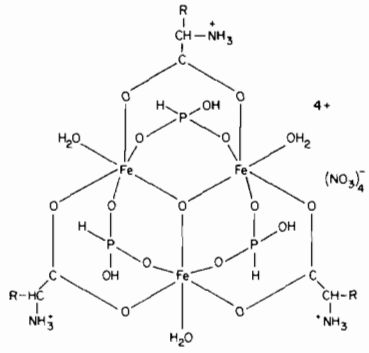

Fig. 2. Schematic representation of the general molecular structure of iron(III)-L-amino acid tris(dihydrogen phosphito) nitrates as deduced by analysis of the physical data presented herein.

acids containing different functionalities. On the basis of analytical, spectral, and magnetic data to be presented below, these complexes have been assigned the general formula, $[Fe_3O(L\text{-amino-acid})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$. For the sake of simplicity the complexes in this work have been identified with the name iron(III)-L-amino acid triphosphito nitrates throughout this paper.

Experimental

Unless otherwise stated, crystalline, A-grade, L-amino acids were used as obtained from Calbiochem. Ferric nitrate nonahydrate was obtained from Malinckrodt (ACS reagent grade), and phosphorus acid was obtained from Fischer (ACS reagent grade). These reagents were used without further purification. Centrifugation was by Sorvall RC2-B Automatic Superspeed Refrigerated Centrifuge (Dupont instruments/Sorvall). The samples were run in polypropylene bottles, 61 X 122 mm (E. I. Dupont de

TABLE I. Elemental Analyses of Iron(III)-L-Amino Acid Triphosphite Nitrates (with Postulated Formulations).

Amino Acid Complex	Element			
	C	H	N	Fe
L-alanine —— found	15.15	3.53	9.76	15.40
calcd for $[Fe_3O(L\text{-alanine})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$	16.78	3.63	9.13	15.61
L-proline —— found	16.70	3.83	8.33	16.74
calcd for $[Fe_3O(L\text{-proline})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$	16.80	3.31	9.80	16.80
L-leucine —— found	19.41	4.70	8.25	14.80
calcd for $[Fe_3O(L\text{-leucine})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$	19.25	4.54	8.73	14.96
L-isoleucine —— found	18.53	4.76	7.42	14.70
calcd for $[Fe_3O(L\text{-isoleucine})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$	19.25	4.54	8.73	14.96
L-phenylalanine —— found	23.01	3.37	6.39	12.70
calcd for $[Fe_3O(L\text{-phenylalanine})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$	24.54	3.40	7.42	12.71
L-histidine —— found	18.48	3.57	16.76	14.24
calcd for $[Fe_3O(L\text{-histidine})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$	18.09	3.26	15.24	14.05
L-serine —— found	11.06	3.71	8.55	16.85
calcd for $[Fe_3O(L\text{-serine})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$	10.35	3.16	9.39	16.08
L-arginine —— found	17.49	4.43	14.33	13.97
calcd for $[Fe_3O(L\text{-arginine})_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$	17.74	4.53	15.77	13.70

TABLE II. Electronic Spectra of Iron(III)-L-Amino Acid Triphosphito Nitrates in the Solid State (Nujol Mull).

Amino Acid Complex	Band Assignment, ν_{max}, cm^{-1}	
L-alanine	10,101	16,393
L-proline	10,101	16,393
L-leucine	10,204	16,528
L-isoleucine	10,309	16,393
L-phenylalanine	10,309	16,129
L-histidine	10,695	16,051
L-serine	10,204	16,129
L-arginine	10,638	16,129

TABLE III. Electronic Spectra of Iron(III)-L-Amino Acid Triphosphito Nitrates in Aqueous Solution.

Amino Acid Complex	Band Assignment, ν_{max}, cm^{-1}	
L-alanine	11,764	22,222
L-proline	11,764	22,988
L-leucine	11,904	22,831
L-isoleucine	12,345	22,272
L-phenylalanine*		
L-histidine	12,269	23,255
L-serine	12,195	23,255
L-arginine	12,195	23,255

*Insoluble in water.

Nemours and Co., Inc.) at room temperature. The iron(III)-L-amino acid triphosphito nitrates derived from L-alanine, L-proline, L-leucine, L-isoleucine, L-phenylalanine, L-histidine, L-serine, and L-arginine were prepared by the general procedure described below.

Method of Preparation

An aqueous solution containing L-amino acid, ferric nitrate nonahydrate, and phosphorous acid in the molar ratio 2:1:0.5 was stirred under reflux at 90 °C for 3 days. The reaction mixture was cooled to room temperature and centrifuged at 10,000 rpm for 2 hr. The supernatant was allowed to evaporate at room temperature. The resulting solid mass was stirred in acetone overnight to remove unreacted ferric nitrate and/or phosphorous acid. The precipitate was washed with acetone and cold ethanol (95%), and air-dried overnight to yield the triphosphito complex.

Elemental Analyses

Elemental analyses were performed by Huffman Laboratories, Inc. and the Chemical and Bacteriological Laboratory of Wyoming Department of Agriculture. The data are presented in Table I with postulated formulations.

Electronic Spectra

Electronic spectra of the triphosphito complexes in the visible and near infrared regions were obtained in aqueous solution using a Cary 14R Spectrophotometer; solid state spectra were obtained by mulling the complexes in nujol and mounting the mulls between the quartz plates. The data are presented in Tables II and III.

Infrared Spectra

Infrared spectra were obtained on an automatic recording, double beam-optical mull IR 10 spectrophotometer from Beckman Instruments Co. The spectra were taken using KBr pellets. Data are presented in Tables IV, V, VI, and VII.

Magnetic Data

Magnetic susceptibility measurements on solid samples were made on a Faraday balance consisting of a Cahn DTL-Electrobalance. The samples were

TABLE IV. Infrared Spectral* Bands of Iron(III)-L-Amino Acid Triphosphito Nitrates.

Amino Acid Complex	Spectral Frequency Assignment, cm^{-1}				
	$\nu_{asym}(NH_3^+)$ and $\nu_{sym}(NH_3^+)$	$\nu_{asym}(H_2O)$ and $\nu_{sym}(H_2O)$	$\nu_{asym}(COO)$	$\nu_{sym}(COO)$	$\Delta\nu(COO)$
L-alanine	$3280-2800^{b,s}$	$3600-3300^{b,s}$	$1620^{b,s}$	$1450^{shp,m}$	170
L-proline		$3600-3320^{b,s}$	$1650^{sh,s}$	$1440^{sh,m}$	210
L-leucine	$3300-2800^{b,s}$	$3600-3350^{b,s}$	$1640^{sh,s}$	$1440^{sh,s}$	200
L-isoleucine	$3200-2800^{b,s}$	$3600-3300^{b,s}$	$1650^{sh,s}$	$1450^{sh,s}$	200
L-phenylalanine	$3260-2800^{b,s}$	$3600-3300^{b,s}$	$1650^{sh,s}$	$1440^{sh,s}$	210
L-histidine	$3200^{b,s}$	$3600-3400^{b,s}$	$1650^{sh,s}$	$1450^{sh,s}$	200
L-serine	$3200-2800^{b,s}$	$3600-3200^{b,s}$	$1650^{shp,s}$	1450^{sh}	200
L-arginine	$3200-2800^{b,s}$	$3600-3360^{b,s}$	$1650^{b,s}$	$1450^{sh,m}$	200

*Abbreviations: shp, sharp; b, broad; sh, shoulder; w, weak; m, medium; s, strong; asym, asymmetric; sym, symmetric.

TABLE V. Infrared Spectral* Bands of Iron(III)-L-Amino Acid Triphosphito Nitrates.

Amino Acid Complex	Spectral Frequency Assignment, cm^{-1}		
	$\nu_1 + \nu_3(NO_3)$	ν(NO)	δ (NO)
L-alanine	2360–2280^{b,w}	1390–1340^{b,s}	830^{shp,w}
L-proline	3360–2300^{b,w}	1370–1350^{b,s}	830^{shp,w}
L-leucine	2360–2300^{b,w}	1390–1360^{b,s}	830^{shp,w}
L-isoleucine	2360–2300^{b,w}	1380–1340^{b,s}	830^{shp,w}
L-phenylalanine	2360–2280^{b,w}	1390–1360^{b,s}	820^{shp,w}
L-histidine	2360–2300^{b,w}	1390–1340^{b,s}	830^{shp,w}
L-serine	2360–2300^{b,w}	1390–1340^{b,s}	830^{shp,w}
L-arginine	2360–2300^{b,w}	1400–1300^{b,s}	820^{shp,w}

*Abbreviations: shp, sharp; b, broad; sh, shoulder; w, weak; m, medium; s, strong; asym, asymmetric; sym, symmetric.

TABLE VI. Infrared Spectral* Bands of Iron(III)-L-Amino Acid Triphosphito Nitrates.

Amino Acid Complex	Spectral Frequency Assignment, cm^{-1}	
	ν(FeO)**	ν(FeO)**
L-alanine	600–500^{b,w}	440–340^{b,w}
L-proline	600–540^{b,w}, 520–460^{b,w}	410–350^{b,w}
L-leucine	600–530^{b,w}	450^{sh,w}, 420–350^{b,w}
L-isoleucine	600–530^{b,w}	450^{b,w}, 430–350^{b,w}
L-phenylalanine	600–540^{b,w}, 480^{sh,w}	440–350^{b,w}
L-histidine	590–540^{b,w}	430–330^{b,w}
L-serine	600–530^{b,w}, 490–460^{sh,w}	530–330^{b,w}
L-arginine	600–500^{b,w}	430–340^{b,w}

*Abbreviations: shp, sharp; b, broad; sh, shoulder; w, weak; m, medium; s, strong; asym, asymmetric; sym, symmetric.
**Further qualification with respect to asymmetric and symmetric Fe–O stretch could not be made.

TABLE VII. Infrared Spectral* Bands of Iron(III)-L-Amino Acid Triphosphito Nitrates.

Amino Acid Complex	Spectral Frequency Assignment, cm^{-1}		
	ν(PH)	ν(PO)	ν(P–OH)
L-alanine	2420^{shp,w}	1150–1030^{b,s}	1030–990^{b,s}
L-proline	2420^{shp,w}	1150–1050^{b,s}	1040–990^{b,s}
L-leucine	2420^{shp,w}	1160–1070^{b,s}	1030–1000^{b,s}
L-isoleucine	2420^{shp,w}	1170–1060^{b,s}	1030–990^{b,s}
L-phenylalanine	2420^{shp,w}	1160–1040^{b,s}	1020–980^{b,s}
L-histidine	2420^{shp,w}	1150–1080^{b,s}	1040–1000^{b,s}
L-serine	2420^{shp,w}	1160–1050^{b,s}	1040–970^{b,s}
L-arginine	2420^{shp,w}	1150–1070^{b,s}	1050–990^{b,s}

*Abbreviations: shp, sharp; b, broad; sh, shoulder; w, weak; m, medium; s, strong; asym, asymmetric; sym, symmetric.

suspended between the poles of an Alpha Scientific Lab., model A 17500M magnet. The sample holder and balance were so designed as to be readily evacuated and purged with helium gas for low temperature work. Power to and regulation of the magnet were provided by an Alpha model AL 7500 power supply and 7500R regulator respectively. The Faraday balance was calibrated with $CoHg(CNS)_4$. Molecular weights used to calculate molar magnetic susceptibilities were estimated from analytical data. Magnetic data for L-amino acid complexes described in this paper are summarized in Table VIII.

TABLE VIII. Magnetic Susceptibilities and Magnetic Moments of Iron(III)-L-Amino Acid Triphosphito Nitrates.

Amino Acid Complex	Temperature (K)	$\chi_M \times 10^6$ (cgsu)	μ_{eff} (BM)	$-J$ (cm^{-1})
L-alanine	294	3,558	2.90	27.8
	80	5,025	1.80	
L-proline	294	3,797	3.00	28.4
	80	5,836	1.94	
L-leucine	294	3,861	3.03	28.1
	80	5,025	1.80	
L-isoleucine	294	3,616	2.92	28.9
	80	4,695	1.74	
L-phenylalanine	294	5,002	3.44	27.2
	80	8,198	2.30	
L-histidine	294	3,177	2.74	40.3
	80	6,199	2.00	
L-serine	294	4,202	3.16	28.5
	80	6,834	2.10	
L-arginine	294	3,235	2.77	40.8
	80	7,500	2.20	

Discussion

Our experience has shown that it is not possible to get correct phosphorus analysis on these complexes by standard methods. Repeated attempts to obtain phosphorus analysis yielded varying values, while no significant change in the values of carbon, hydrogen, nitrogen, and iron was observed. This observation agrees with the findings of Podlaha *et al.* [13] and Puri *et al.* [14, 15] who encountered similar difficulties with complexes derived from chromium(III) or iron(III), and phosphorous acid. Along these lines, we concur with the suggestion made by Podlaha *et al.* [13, 23] that phosphorous acid is ligated to the chromium(III) in a bidentate fashion, and that this suggestion also holds for complexes containing iron(III) and phosphorous acid [14, 15]. Experimentally determined analytical values for the postulated formulations of the complexes described in this work differ from the calculated values; similar deviations have been frequently encountered in analysis of polynuclear oxobridged iron(III) complexes, both by ourselves and others [9–11, 27, 31, 36]. The elemental analyses are satisfactory with respect to the amino acid/iron ratio. It is worthwhile pointing out that the conditions for incorporating L-amino acid and phosphorous acid simultaneously into the $[Fe_3O]^{7+}$ unit were arrived at only after considerable experimentation and that the molar ratio of L-amino acid and phosphorous acid to ferric nitrate described in the experimental section bears no relationship to the actual stoichiometric composition of these species in the iron(III) complexes in this work.

The solid state spectra of the triphosphito complexes consist of two bands at *ca.* 10,000 cm^{-1} and 16,000 cm^{-1} (Table II). The spectra are characteristic of compounds containing $[Fe(III)O_6]_{oct}$ unit(s) and the trimeric species, $[Fe_3O]^{7+}$ [10, 11, 16]. The absorption band at *ca.* 10,000 cm^{-1} may be attributed to $^6A_1 \rightarrow {}^4T_2$ transition and the one at 16,000 cm^{-1} may be attributed to a $^6A_1 \rightarrow {}^4T_2$ transition. The electronic spectra of the complexes in aqueous solution exhibit bands due to transitions $^6A_1 \rightarrow {}^4T_1$ and $^6A_1 \rightarrow {}^4T_2$ at higher energy regions, 11,000–12,000 cm^{-1} and 20,000–22,000 cm^{-1} respectively (Table III). The higher energy shift of the two characteristic bands may be due to greater splitting of the t_{2g} and e_g levels in the cubic ligand field by the increased polarity of the solvent; similar results were obtained for iron(III)-L-amino acid perchlorates [10] and nitrates [11]. The close similarity of the electronic spectral data of the triphosphito complexes in this work with that of the known iron-(III)-L-amino acid perchlorates [9, 10] and nitrates [11], and iron(III)-carboxylates [27] (Table IX) supports our formulation of the complexes in this work as shown in Fig. 2.

The infrared spectra of the complexes under consideration show prominent absorptions in the region 2800–3300 cm^{-1} and *ca.* 1650 and *ca.* 1450 cm^{-1} (Table IV); the former has been attributed to the asymmetric and symmetric stretching modes [10, 11] due to a NH_3^+ function present in the L-amino

TABLE IX. Comparison of the Spectral Bands of the Known Complexes Containing the $[Fe_3O]^{7+}$ Unit with that of Ferritin.‡

Complex	Band Assignment, ν_{max}, cm^{-1}	
$[Fe_3O(L\text{-}phe^*)_6(H_2O_3)](ClO_4)_7(HClO_4)_2$ [a]	10,416	16,260
$[Fe_3O(L\text{-}phe)_6(H_2O)_3](NO_3)_7$ [b]	10,204	16,260
$[Fe_3O(Cl\cdot CH_2COO)_6(H_2O)_3]Cl\cdot 5H_2O$	10,300	16,000
$[Fe_3O(HPO_3)_3(H_2O)_9]Cl\cdot 3H_2O$ [d]	10,416	16,393
$[Fe_3O(L\text{-}phe)_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$ [e]	10,309	16,129
Ferritin [f]	10,900	–

‡ Abbreviations: [a] Reference 9. [b] Reference 11. [c] Reference 27. [d] Reference 15. [e] This work. [f] Reference 16, only one band reported. *phe = phenylalanine.

acid ligands, and the latter two to the asymmetric and symmetric modes [9–11] of the carboxylate function of L-amino acid ligated to the irons in the complexes. The presence of these bands demonstrates that L-amino acid ligands in these complexes are present as zwitterions. The $\Delta\nu$(COO) between the two stretching modes of the carboxyl function is of the order of 200 cm^{-1} (Table IV). Tucker *et al.*, in their study of the iron(III)-L-amino acid perchlorates [9] and Puri *et al.* in their study of iron-(III)-L-amino acid perchlorates [10] and nitrates [11], have observed similar values of $\Delta\nu$(COO) which is characteristic of a carboxyl function coordinated to adjacent irons in a bidentate fashion in complexes containing $[Fe_3O]^{7+}$ nucleus [33]. The spectra of the triphosphito complexes show broad and strong absorption bands in the region 3000–3600 cm^{-1} (Table IV); these bands correspond to asymmetric and symmetric OH stretching modes [17, 18] of water molecules either coordinated to the irons and/or present in the lattice network of the complexes. The FeO stretches in the spectra of complexes of iron(III) octahedrally surrounded by oxygens have been described elsewhere [37–39]. Recently Puri *et al.* [14] described in detail the nature of FeO stretches in the infrared spectra of octahedral complexes in which phosphorous acid is ligated to chromium(III) and iron(III) in a bidentate fashion. The FeO stretches in the spectra of the complexes in this work were found in the regions 500–520 cm^{-1} and 450–350 cm^{-1} (Table VI) and are typical of similar FeO stretch frequencies found in the spectra of iron(III)-L-amino acid perchlorates [9, 10] and nitrates [11] containing the $[Fe_3O]^{7+}$ unit. The infrared spectra of the complexes in this work also exhibit three bands at *ca.* 2360 cm^{-1}, *ca.* 1380 cm^{-1}, and 830 cm^{-1} (Table V); these have been attributed to a combination mode $\nu_1 + \nu_3(NO_3)$, the asymmetric NO stretching mode, and NO bending mode respectively [19, 22]. It is well known that phosphorous acid forms two series of compounds of the type $O{=}PH(OR)_2$ and $(P(OR)_3$. The infrared spectrum of the former possesses very characteristic absorption bands in the region 1200–1300 cm^{-1} due to P=O stretch and at *ca.* 2400 cm^{-1} due to PH stretch [24, 25]. The infrared spectrum of $P(OR)_3$ is devoid of absorption bands characteristic of the presence of either P=O function or the PH function. If phosphorus acid acts as a bidentate ligand, then it could do so by two different modes of ligation to the metal ion, leaving the P=O and PH functions intact to be acid could be involved in ligation in such a way as to transfer two units of negative charge to the metal ion, leaving the P=O and pH functions intact to be seen in the infrared spectrum, or (b) the phosphorous acid could be involved in ligation to the metal atom, in much the same way as the carboxyl group of L-amino acid, *i.e.*, through the O=P–OH function thus transferring only one unit of negative charge to the metal ion. The latter type of coordination, involving metal ion and phosphorous acid, would then leave the PH and one of the POH functions intact and the infrared spectra of complexes containing the described mode of coordination would not exhibit the absorption bands, due to the presence of a P=O function in the molecule. Recent studies of Puri *et al.* described the results of infrared spectral investigations of the model complexes, iron(III) tris(monohydrogen phosphito)chloride [15] (phosphorus acid acts as a bidentate ligand as described in (a) above), and hydrogen tris(monohydrogen phosphito)ferrate-(III) and chromate(III) [14] (phosphorous acid acts as a bidentate ligand as described in (b) above), which support the above conclusions. It is in this latter type of bonding that phosphorous acid is involved in the triphosphito complexes in question. The infrared spectra of the triphosphito complexes do not exhibit absorption in the region 1200–1300 cm^{-1} but they show broad and intense absorption bands in the lower energy region 1050–1150 cm^{-1} (Table VII), thus indicating that a considerable amount of the double bond character of the P=O function from the phosphorous acid is removed on coordination with the irons. The infrared spectra of triphosphito complexes also contain weak absorption bands at *ca.* 2400 cm^{-1} and broad intense absorption bands in the region

TABLE X. Comparison of the Magnetic Data of the Known Complexes Containing the $[Fe_3O]^{7+}$ Unit with that of Ferritin.

Complex	Temperature (K)	μ_{eff} (BM)	$-J$ (cm^{-1})
$[Fe_3O(L\text{-}phe^*)_6(H_2O)_3]ClO_4)_7\cdot(HClO_4)_2$ [a]	294	3.42	25.0
	80	2.01	
$[Fe_3O(L\text{-}phe)_6(H_2O)_3](NO_3)_4$ [b]	294	3.47	27.0
$[Fe_3O(Cl\cdot CH_2COO)_6(H_2O)_3]Cl\cdot 5H_2O$ [c]	296.5	3.30	27.0
	84.5	2.01	
$[Fe_3O(HPO_3)_3(H_2O)_9]Cl\cdot 3H_2O$ [d]	294	3.77	18.2
$[Fe_3O(L\text{-}phe)_3(H_2PO_3)_3(H_2O)_3](NO_3)_4$ [e]	294	3.44	27.2
	80	2.30	
Ferritin [f]	300	3.81	30

[a] Reference 9. [b] Reference 11. [c] Reference 27. [d] Reference 15. [e] This work. [f] Reference 28. *phe = phenylalanine.

900–1030 cm^{-1} (Table VII); the former is characteristic of the presence of PH function and the latter of the presence of POH function [24, 25] in these complexes. From the infrared spectral studies, it can therefore be inferred that the molecular structure of the triphosphito complexes in this work can be adequately represented by Fig. 2. This structural representation is strongly supported by the elemental analyses which required the charge balance shown in these structures. The infrared spectral studies and the analytical data, coupled with the fact that phosphorus is held tenaciously in these complexes (as shown by our inability to get correct analyses on the phosphorus content of these complexes), support our contention that phosphorous acid acts as a bidentate and not monodentate ligand in these complexes.

Magnetic measurements on the complexes in question were made at 294 K and 80 K; values of the exchange integral, $-J$, were calculated by the method of Earnshaw *et al.* [26]. The magnetic moments of these complexes were found to be in the range 2.78–3.43 BM at 294 K decreasing to 1.80–2.1 BM at 80 K (Table VIII). These observations strongly suggest that the complexes are antiferromagnetic in character; this is further supported by the values of $-J$ in the range 40.8–27.8 cm^{-1} for the complexes. The value of magnetic moment and exchange integral for the complexes in this work compare favorably with those of the known trinuclear oxobridged iron(III) perchlorates [9, 10] and nitrates [11], and iron(III) carboxylates [26, 27] (Table X). X-ray analysis of some of the iron(III)-L-amino acid perchlorates [28] containing the trimeric species $[Fe_3O]^{7+}$, has shown that the Fe–Fe distance in such complexes is *ca.* 3.29 Å. Therefore, direct overlap of metal–metal orbitals is unlikely to contribute significantly to the exchange mechanism. Rather, exchange must occur by the overlap of metal d-orbitals with the bridging oxygen p-orbitals. It has been suggested [29] that in a linear superexchange for the d^5–d^5 system, the direct overlap between e_g(Fe) and P_y(O) orbitals significantly contributes to the overall antiferromagnetism. It is therefore not surprising that a value of 95 cm^{-1} for the exchange integral, $-J$, has been reported for the complexes [30] containing linear Fe(III)–O–Fe(III) linkages. On the other hand in dialkoxobridged iron(III) complexes [31–33] where the geometrical restrictions impose an angle of *ca.* 90° on the Fe(III)–O–Fe(III) bridge metal $d\pi$ orbitals, and where oxygen $p\pi$ orbitals are in less favorable spatial orientation for significant overlap, a value of *ca.* 10 cm^{-1} has been reported for the exchange integral. The Fe(III)–O–Fe(III) angle in some of the known iron(III)-L-amino acid perchlorates [28], containing the unit $[Fe_3O]^{7+}$, has been found to be *ca.* 120° and a $-J$ value of *ca.* 30 cm^{-1} for the perchlorate complexes is thus expected on the grounds that a substantial spin coupling between metal $d\pi$ and oxygen $p\pi$ orbitals is possible because of the equilateral geometry of the $[Fe_3O]^{7+}$ unit; this has been substantiated by experiment [9]. Since the value of the exchange integral, $-J$, in the triphosphito complexes is in close agreement with those of known complexes [9–11, 26, 27] containing the nucleus $[Fe_3O]^{7+}$ (Table X), their molecular structures should also be very similar. The exchange integral values for complexes in this work were obtained by computations based on the assumption that there is an equivalent coupling between two adjacent irons. However, in the absence of X-ray studies this assumption could not be verified.

Based on the spectral and magnetic properties of the triphosphito complexes, it can be concluded that

the triphosphito complexes (Fig. 2) retain the features of the gross molecular structure of the known iron(III)-L-amino acid perchlorates and nitrates, and iron(III) carboxylates. In summary the evidence supports the conclusion that iron(III) L-amino acid complexes, containing the unit $[Fe_3O]^{7+}$, remain important contenders among the models [9–11, 34, 35] proposed for the ferritin iron core. The presence or absence of phosphorus in the complexes derived from iron(III) and L-amino acids has a minimal effect on their spectral and magnetic properties and the oxygen containing ligands in general have minimal effect on the diagnostic spectral and magnetic properties intrinsically associated with the $[Fe_3O]^{7+}$ unit (Tables IX and X). This study corroborates the view held by several investigators [2, 3, 8], namely that the presence of phosphorus in the ferritin iron core plays little role in the structural organization of the ferritin iron core. However, this work has no bearing on the importance of the role of phosphorus in ferritin toward its physiological properties.

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