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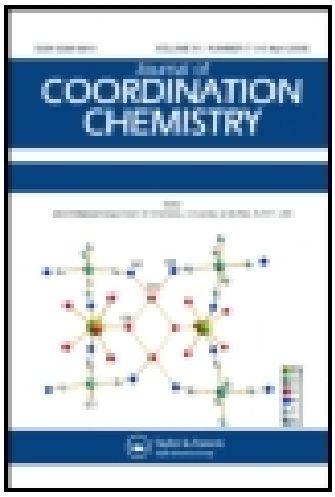

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

PREPARATION AND PROPERTIES OF TRINUCLEAR OXOBRIDGED IRON(III)-L-AMINO PERCHLORATES: AMINO ACIDS WITH REACTIVE R GROUPS

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Published online: 03 Jan 2007.

To cite this article: Rajinder N. Puri, R. Owen Asplund & Smith L. Holt (1981) PREPARATION AND PROPERTIES OF TRINUCLEAR OXOBRIDGED IRON(III)-L-AMINO PERCHLORATES: AMINO ACIDS WITH REACTIVE R GROUPS, Journal of Coordination Chemistry, 11:2, 125-131, DOI: 10.1080/00958978108079057

To link to this article: http://dx.doi.org/10.1080/00958978108079057

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J. Coord. Chem., 1981, Vol. 11, pp. 125–131
0095-8972/81/1102-0125 $06.50/0

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PREPARATION AND PROPERTIES OF TRINUCLEAR OXOBRIDGED IRON(III)-L-AMINO PERCHLORATES: AMINO ACIDS WITH REACTIVE R GROUPS.†

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(*Received March 20, 1980; in final form March 9, 1981*)

Trinuclear oxobridged iron(III)-L-amino acid perchlorates derived from a variety of L-amino acids, i.e. hydrophobic, aromatic, hydroxy, and sulfur-containing L-amino acids have been prepared, and their spectral and magnetic properties examined. The results support the view that complexes containing the unit $[Fe_3O]^{7+}$ are the preferred chemical entities under the described reaction conditions.

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INTRODUCTION

Among all the models proposed[1,2,3,15] for the structure of the ferritin iron core, iron(III)-L-amino acid perchlorates is one of the most attractive. Studies previously carried out on iron(III)-L-alanine,[4] iron(III)-glycine,[5] and related complexes of amino acids with aliphatic R groups show that the crystal structure of these complexes is analogous to that found in $[Fe_3O(OAC)_6(H_2O)_3](ClO_4)$,[6] and similar transition metal complexes.[7–10] The overall structure (Figure 1) of the known iron(III)-L-amino acid complexes consists of a central oxygen bonded to three iron atoms in approximately the same plane. Pairs of iron atoms are bridged by two amino acids through the oxygens of the carboxyl groups. The sixth coordination site is occupied by the oxygen of a water molecule. A very important feature of the structures is that amino acid ligands exist as Zwitterions and the amino nitrogen does not participate in ligation. The perchlorate ions act as counterions to the positively charged nitrogens in the amino acid residues.

The study has been extended to trinuclear oxobridged iron(III)-L-amino acid complexes of aromatic, acidic, basic, hydroxy, and sulfur-containing amino acids to determine the effect, if any, of the side chain of the amino acid residues on the overall coordination of these ligands to irons in the trinuclear oxobridged complexes.

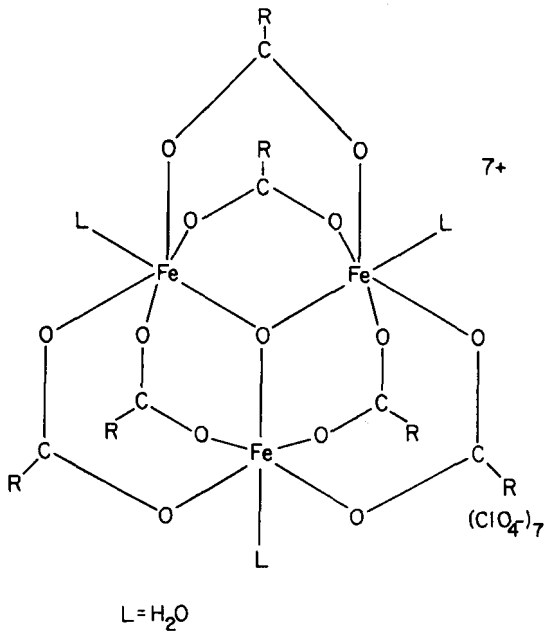

FIGURE I Generalized molecular structure of iron(III)-L-amino acid perchlorates as dediced from physical properties.

†Paper No. 6 in a series. See bibliography for preceding papers.

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EXPERIMENTAL

Unless otherwise stated, crystalline, A-grade, L-amino acids were used as obtained from Calbiochem. Ferric perchlorate, hydrated yellow $Fe(ClO_4)_3 \cdot 6H_2O$, was obtained from G. Fredric Smith Chemical Company and used as obtained. Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, CO and Bacteriological Laboratory of the Wyoming Department of Agriculture, Laramie, WY. Iron analyses were run using a standard colorimetric method,[11] but with the proline complex as a reference standard. Analyses were run in quadruplicate and are reported as a mean with a standard deviation.

All solution electronic spectra were run in anhydrous methanol using a Cary 14R spectrophotometer; solid state spectra were run by mulling the complexes in nujol and mounting the mulls between quartz plates. Infrared spectra were obtained from KBr pellets on Beckman IR 10 infrared spectrophotometer. Magnetic susceptibility measurements on solid samples were run on a Faraday balance consisting of Cahn DTL-Electrobalance. The samples were 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 Alpha model 7500 R regulator respectively. The Faraday balance was calibrated with $CoHg(CNS)_4$. Molecular weights were estimated from analytical data.

The amino acid complexes derived from L-glutamic acid, L-phenylalanine, L-histidine, L-tryptophan, S-benzyl-L-cysteine, L-arginine, L-threonine, and L-hydroxyproline were prepared according to the following general method. Aqueous solutions of the L-amino acids and ferric perchlorate were mixed in molar ratio of 2:1 and/or 1:1. In some cases crystalline complexes could be isolated by evaporation of the above reaction mixture at atmospheric conditions and room temperature. For those amino acids which were sparingly soluble, aqueous suspensions were used. If the product obtained was a gummy solid, maceration with nitromethane or acetonitrile usually yielded a powdered solid. All attempts to prepare the iron(III)-L-cysteine complex by the above methods resulted only in the formation of cystine. In the case of the complexes derived from L-histidine and L-phenylalanine, the pH of the reaction mixture was adjusted to 1.0 with 30% aqueous perchloric acid solution.

Precaution!

In the case of trytophan, the reaction mixture was allowed to evaporate at room temperature in the dark. A very small portion of the resulting solid was taken out as needed, by extremely gentle scraping. This complex proved to be readily explosive on standing in light, as we encountered it.

RESULTS AND DISCUSSION

Analysis

The results of the elemental analysis of the prepared complexes is shown in Table I together with the formulation which appears to best fit the analytical data. We have experienced difficulty in obtaining precise analytical data for carbon, hydrogen, nitrogen and chlorine in compounds of this type. Deviations, up to five per cent, from calculated values for these elements in polynuclear iron complexes have been reported by several investigators.[3,12–14] Similar difficulty was also experienced with the iron analyses, but when the iron-proline complex was used as a reference standard, values were obtained which showed good precision. The detailed structure of the iron-proline complex is known from X-ray crystallographic analysis.[4,5] The data for iron analyses fit the postulated formulation in all cases.

Electronic Spectra

The near infrared and visible electronic spectrum for each of these complexes has been recorded in the solid state and solution. The results are presented in Table II. For the solid state and for methanolic solution, each spectrum consists of two characteristic absorption bands at ca. 10,000 cm^{-1} and ca. 16,000 cm^{-1}. The solid state electronic spectra of compounds containing the $[Fe^{3+}O_6]_{oct}$ and $[Fe^{3+}O_4]_{tet}$ units have been described.[16] The electronic spectra of the compounds containing $[Fe^{3+}O_4]_{tet}$ do not exhibit absorption bands at ca. 10,000 and ca. 16,000 cm^{-1}. These two absorption bands are very characteristic of compounds containing the $[Fe^{3+}O_6]_{oct}$ unit and correspond to $^6A_1 \rightarrow {}^4T_1(^4G)$ and $^6A_1 \rightarrow {}^4T_2(^4G)$ transitions. In the solid state, electronic spectra of the compounds containing $[Fe^{3+}O_6]_{oct}$ exhibit the high energy bands associated with $^6A_1 \rightarrow {}^4A_1(^4G)$ and/or $^4E(^4G)$ and $^6A_1 \rightarrow {}^4T_2(^4D)$ transitions. Further more, the $^6A_1 \rightarrow {}^4T_1(^4G)$ transitions also vary with the

TABLE I
Elemental analyses for iron(III)-L-amino acid perchlorates together with formulation postulated from best fit to analysis.

Amino acid complex†	Element					
	C	H	N	Cl	S	Fe‡
L-glutamic acid — found	17.40	3.81	3.97	10.43		8.90
calcd for $[Fe_3O(L\text{-glu})_6 3H_2O](ClO_4)_7(HClO_4)_2$	17.80	2.97	4.10	12.30		8.87 ± 0.11
L-phenylalanine — found	31.00	4.30	4.10	15.60		8.20
calcd for $[Fe_3O(L\text{-phe})_6 3H_2O](ClO_4)_7(HClO_4)_2$	30.50	3.48	3.95	15.03		8.14 ± 0.06
L-histidine — found	16.01	2.35	9.20	16.95		6.07
calcd for $[Fe_3O(L\text{-his})_6 3H_3O](ClO_4)_7(HClO_4)_6$	16.01	3.26	8.48	15.64		5.88 ± 0.23
S-benzyl-L-cysteine — found	32.7	3.82	3.82	11.3	8.72	7.61
calcd for $[Fe_3O(S\text{-benz-L-cys})_6 3H_2O)(ClO_4)_7$	31.54	4.06	3.42	11.2	8.60	7.55 ± 0.05
L-arginine — found	20.80	4.42	15.72	13.90		6.09
calcd for $[Fe_3O(L\text{-arg})_6 3H_2O](ClO_4)_7(HClO_4)_2$	19.82	4.22	15.42	14.60		6.21 ± 0.31
L-threonine — found	14.48	3.76	4.12	15.59		7.95
calcd for $[Fe_3O(L\text{-thr})_6 3H_2O](ClO_4)_7(HClO_4)_3$	14.70	3.23	4.3	18.20		8.20 ± 0.44
L-hydroxyproline	19.99	3.58	4.25	15.75		8.65
calcd for $[Fe_3O(L\text{-hyp})_6 3H_2O](ClO_4)_7HClO_4$	19.70	3.35	4.60	15.60		8.72 ± 0.38

†The explosive nature of the iron(III)-L-trytophan complex precluded analysis.
‡Iron determination was by the standard phenanthroline colorimetric method using the iron–proline complex as a reference standard. Values are means of quadruplicate analyses plus or minus the standard deviation.

TABLE II
Electronic spectral bands of iron(III)-L-amino acid perchlorates.

Amino acid complex	Condition	Band assignment, ν_{max}, cm^{-1} (ε, lit $mole^{-1}$ cm^{-1}/Fe^{3+})	
		$^6A_1 \rightarrow {}^4T_1$	$^6A_2 \rightarrow {}^4T_2$
L-glutamic acid	nujol	10,309	16,129
	methanol	10,362 (1.42)	16,129
L-phenylalanine	nujol	10,416	16,260
	methanol	10,204	16,129 (6.42)
L-histidine	nujol	10,416	16,260
	methanol	10,256 (.290)	16,129 (6.58)
S-benzyl-L-cysteine	nujol	10,309	16,393
	methanol	10,256	16,666
L-arginine	nujol	10,416	16,260
	methanol	10,416	15,151
L-threonine	nujol	10,416	16,129
	methanol	10,362	16,393
L-hydroxyproline	nujol	10,416	16,260
	methanol	10,309 (.472)	16,393 (6.5)
L-tryptophan	methanol	10,638	15,625

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oxygen-containing ligands in the cubic ligand field.[17] It has also been established[18,19] that the solid state electronic spectra and the methonolic solution electronic spectra of the complexes of the type $[Fe_3O(L\text{-alanine})_6 3H_2O](ClO_4)_7$ and $[Fe_3O(OAC)_6 3H_2O]ClH_2O$ are very similar. Thus, the essential features of their molecular structure in the solid state are preserved in solution. The molar extinction coefficients reported in Table II appear to be rather high for spin-forbidden transitions; however, similar high intensity bands have been reported in other polynuclear iron(III) complexes.[18,19] Schugar *et al.* have suggested[38] that the intensity enhancement in the electronic spectra of oxobridged iron(III) dimers is related to their antiferromagnetic character. The antiferromagnetic character of these complexes probably results from extensive orbital overlap which should also yield increased intensity of absorption. Ferguson *et al.*[20] have noted a similar phenomenon in their study of the electronic spectral bands in several Mn^{2+} (high spin d^5 configuration) complexes. The fact that the electronic spectral data of iron(III)-L-amino acid complexes, in this study, very closely resemble the spectra of the related trinuclear iron(III)-carboxylates[19] and the known iron (III)-L-amino acid perchlorates described elsewhere[3,18] supports the proposed structures.

Infrared Spectra

The infrared spectra of the iron(III)-L-amino acid complexes prepared have been recorded and are presented in Tables III, IV and V. In the iron(III)-L-amino acid complexes under consideration, water is present both as lattice water and/or coordinated water. There is, however, no sharp distinction between the expected spectral features resulting from the two. In general, water absorbs at 3500–3200 cm^{-1} corresponding to the antisymmetric and symmetric O–H stretching modes and at 1630–1600 cm^{-1} corresponding to the HOH bending modes.[22–24] In the spectra of these complexes, the region 3500–3300 cm^{-1} also contains modes for the asymmetric carboxyl stretch. In the spectra of the iron(III)-L-amino acid perchlorates examined, the N–H asymmetric and symmetric stretching frequencies appear in the region 3150–2880 cm^{-1} whereas in the spectra of the amino acids the asymmetric and symmetric stretching modes appear in the region 3130–3030 cm^{-1}.[26] In the spectra of the L-amino acid complexes the lowering of frequencies of the corresponding N–H stretching modes of theNH_3^+ function may be due to the hydrogen bonding between the NH_3^+ group of the Zwitterionic amino acids with perchlorate anions acting as counterions. All the amino acids show two bands in the region 1660–1590 cm^{-1} and 1550–1480 cm^{-1} corresponding to the asymmetric and symmetric bending modes of NH_3^+.[25] The spectra of all the amino acid complexes examined in this study show absorptions at ca. 1610 cm^{-1} and ca. 1490 cm^{-1}. It has been pointed out[27] that all the amino acids have a characteristic absorption band of medium intensity in the region 1350–1300 cm^{-1}. The complexes examined show a similar absorption; it is attributable to either the C–N stretching mode and/or the C–H bending mode. The asymmetric and symmetric carboxylate stretching modes in the spectra of the complexes are located at ca. 1640 cm^{-1} and ca. 1440 cm^{-1} respectively. The $\Delta\nu$ between the two stretching modes in the spectra of the complexes examined in this study is of the order of 200 cm^{-1} and is compatible with the observation made by Tucker *et al.*[3] in connection with the known iron(III)-L-amino acid perchlorates in which carboxylate function bridges the two adjacent irons in

TABLE III
Infrared spectral bands† of iron(III)-L-amino acid complexes.

Amino acid complex	Spectral frequency assignment, cm^{-1}			
	$\nu_{as}(NH_3^+)$ and $\nu_{sym}(NH_3^+)$	$\delta_{as}(NH_3^+)$	$\delta_{sym}(NH_3^+)$	ν(C—N) and/or δ(CH)
L-glutamic acid	$3000–2900^{b,s}$	1605^{m}	$1500^{shp,m}$	$1300^{shp,s}$
L-phenylalanine	$3050–2850^{b,s}$	1610^{m}	$1490^{shp,m}$	$1345^{shp,s}$
L-histidine	$3150–2900^{b,s}$	1610^{m}	$1490^{shp,m}$	$1350^{shp,s}$
S-benzyl-L-cysteine	$2900–2800^{b,s}$	1605^{m}	$1490^{shp,m}$	$1300^{shp,s}$
L-arginine	$3100–2960^{b,s}$	$1590–1600^{m}$	$1480^{shp,m}$	$1330^{shp,s}$
L-threonine	$3100–2960^{b,s}$	1610^{m}, 1620^{m}	$1500–1490^{m}$	$1300^{shp,s}$
L-hydroxyproline	$3260–2960^{b,s}$	1590^{s}	$1470–1460^{m}$	$1300^{b,w}$
L-tryptophan	$3200–2950^{b,s}$	1605^{s}	1485^{m}	$1300^{shp,s}$

†Abbreviations: shp, sharp; b, broad; w, weak; m, medium; s, strong; as, asymmetric; sym, symmetric.

TABLE IV
Infrared spectral bands† of iron(III)-L-amino acid complexes.

Amino acid complex	Spectra frequency assignment, cm^{-1}			
	$\nu_{as}(H_2O)$ and $\nu_{syn}(H_2O)$	$\nu_{as}(COO)$	$\nu_{sym}(COO)$	$\Delta\nu$
L-glutamic acid	$3500–3400^{b,s}$	$1640^{shp,s}$	$1440^{shp,s}$	200
L-phenylalanine	$3480–3280^{b,s}$	$1660^{shp,s}$	$1440^{shp,s}$	200
L-histidine	$3600–3260^{b,s}$	$1645^{shp,s}$	$1440^{shp,s}$	205
S-benzyl-L-cysteine	$3550–3350^{b,s}$	$1650^{shp,s}$	$1440^{shp,s}$	210
L-arginine	$3460–3360^{b,s}$	$1640^{b,s}$	$1450^{shp,m}$	190
L-threonine	$3500–3300^{b,s}$	$1645^{shb,s}$	1440^{m}	205
L-hydroxyproline	$3500–3300^{b,s}$	$1640^{shp,s}$	1450^{m}	190
L-tryptophan	$3500–3300^{b,s}$	$1630^{shp,s}$	1440^{m}	190

†Abbreviations: shp, sharp; b, broad; w, weak; m, medium; s, strong; as, asymmetric; sym, symmetric.

TABLE V
Infrared spectral bands† of iron(III)-L-amino acid perchlorates.

Amino acid complex	Spectral frequency assignment, cm^{-1}			
	$\nu_3(ClO_4)$	$\nu_4(ClO_4)$	ν(FeO)‡	ν(FeO)‡
L-glutamic acid	$1150–1140^{b,s}$	$620^{shp,m}$	$575–560^{b,w}$	$410^{b,w}$
L-phenylalanine	$1150–1070^{b,s}$	$620^{shp,m}$	$550^{b,w}$	$405^{shp,m}$
L-histidine	$1150–1050^{b,s}$	$620^{shp,m}$	$570^{b,w}$	$440^{shp,w}$, $400^{b,w}$
S-benzyl-L-cysteine	$1140–1030^{b,s}$	$620^{shp,m}$	$570–560^{sh,w}$	$430–410^{b,w}$
L-arginine	$1130–1060^{b,s}$	$620^{shp,m}$	520^{w}, 540^{w}	$460–410^{b,w}$
L-threonine	$1150–1060^{b,s}$	$620^{shp,m}$	$550^{b,w}$	$450^{shp,w}$, $410^{b,w}$
L-hydroxyproline	$1130–1010^{b,s}$	$620^{shp,m}$	$510^{b,m}$	$380^{b,w}$
L-tryptophan	$1150–1010^{b,s}$	$620^{shp,m}$	$590–560^{b,w}$	$410^{shp,m}$

†Abbreviations: shp, sharp; b, broad; w, weak; m, medium; s, strong.
‡Further qualification with respect to asymmetric and symmetric Fe—O stretch could not be made.

the $[Fe_3O]^{7+}$ unit. It is important to mention that both the asymmetric and symmetric carboxylate stretches are shifted to a higher energy region and this observation seems to corroborate the findings of other workers.[28,29] However, in the absence of X-ray diffraction data and normal coordinate analysis on the models of the complexes, the reason for the higher energy shift of both the carboxylate frequencies would be speculative. The absorption bands at ca. 1100 cm^{-1} and ca. 620 cm^{-1} in the spectra correspond to ν_3 and ν_4 vibrational modes of the ClO_4^- ion which belongs to the T_d symmetry group.[30] The low energy region 800–300 cm^{-1}, in the infrared spectra of the iron(III)-L-amino acid complexes is the expected region of observation of bands due to the Fe–O stretching modes. Griffith[31] has suggested that $\nu_{as}(Fe_3O)$ should occur in the region 600–500 cm^{-1}. Long *et al.*[19] have assigned a broad band of moderate intensity at ca. 520 cm^{-1} to the $\nu_{as}(Fe_3O)$ in the iron(III)-acetate complex. In the trivalent metal series, Hancock and Thornton[32] found that ν_{11} (M–O stretching) follows the same trend as the crystal field stabilization energies (CFSE) of the metals. Gugita *et al.*[33] have assigned the absorption at 528 and 366 cm^{-1} to the Fe–O stretching in $K_3[Fe(OX)_3]\cdot 3H_2O$. Mikani *et al.*[34] performed normal coordinate analysis on the 1:3 (octahedral) models of various acetylacetonate complexes and assigned bands of 664, 559, 443, and 298 cm^{-1} to the Fe–O stretching in the complex $Fe(acac)_3$. Nakamoto *et al.*[35] have shown that the band at 300 cm^{-1} in the spectrum of $Fe(acac)_3$ displayed the maximum shift upon isotopic substitution and was accordingly assigned the Fe–O stretch. Smaller shifts were observed for the bands appearing at 436, 511,

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562, and 655 cm^{-1}. Tucker *et al.*,[3] more recently, assigned the band at 570 cm^{-1} to the $\nu_{as}(Fe_3O)$. This band is observed in the spectra of all the iron(III)-L-amino acid perchlorates. The spectra of the iron(III)-L-amino acid perchlorates in this study contain two bands of weak intensity in the regions 575–510 cm^{-1} and 440–350 cm^{-1} which are assigned to the Fe–O stretches in these complexes. Further qualification with regard to the specific assignments must await appropriate isotopic substitution data.

Magnetic Properties

The magnetic measurements on the iron(III)-L-amino acid perchlorate were made at 294°K and 80°K using a Faraday balance and are presented in Table VI. Values of the exchange integral, $-J$, were calculated using the method suggested by Earnshaw *et al.*[21] The magnetic moments of all the iron(III)-L-amino acid complexes examined are in the range 2.6–3.6 BM at 294°K, decreasing to ca. 2 BM at 80°K. This shows that these complexes are antiferromagnetic consistent with a value of ca. 30 cm^{-1} for the exchange integral. The data presented in Table VI compare favorably with that for the known trinuclear iron(III)-carboxylates[19] and known iron(III)-L-amino acid perchlorates.[3] The Fe–Fe distances in the known iron(III) complexes[5] containing the $[Fe_3O]^{7+}$ unit are ca. 3.29 Å. The contribution of direct metal-metal orbital overlap to the exchange mechanisms is considered small. Therefore, the exchange must occur via overlap of metal d orbitals with the bridging oxygen orbitals, a superexchange pathway. Ginsberg[36] has discussed the superexchange theories of Anderson and Goodenough in some detail. In the case of a linear superexchange for a d^5–d^5 system, the direct overlap between e_g(Fe) and P_y(O) orbitals significantly contributes to overall antiferromagnetism;[37] a valueof 95 cm^{-1} for the exchange integral, $-J$ has been reported[38] for a number of iron(III) complexes containing linear Fe–O–Fe linkages. In dialkoxo-bridged dimers of iron(III) where Fe–O – Fe angles approach 90° and where oxygen π-orbitals are available to a lesser extent, a less favorable system for orbital interaction, values of ca. 10 cm^{-1} have been reported[39,40] for the exchange integral. The Fe–O–Fe bond angles in some of the known iron(III)-L-amino Acid perchlorates have been found[5] to be very nearly 120°; the $-J$ value of ca. 30 cm^{-1} for the complexes under consideration support the conclusion that substantial spin coupling occurs through orbital overlap via the bridging oxygen. Since the value of the exchange integral in these complexes is in close agreement with those of the known trinuclear iron(III)-L-amino acid perchlorates[3] and trinuclear iron(III)-carboxylates,[19,21] their molecular structures should also be very similar. This evaluation of the exchange integral in this study has been made on the assumption that there is equivalent coupling between iron atoms 1 and 2 and atoms 2 and 3. The validity of this assumption can not be verified in the absence of X-ray structural analysis.

The spectral and magnetic properties of the trinuclear oxobridged iron(III)-L-amino acid complexes in this study support the conclusions of Tucker *et al.*[3] concerning similarly constituted known iron(III)-L-amino acid complexes: (a) the amino

TABLE VI

Magnetic susceptibility per iron atom and magnetic moment per iron atom of trinuclear iron(III)-perchlorates.

Amino acid complex	Temperature (°K)	Molar susceptibility $\chi_M \times 10^6$ (cgsu)	Magnetic moment μ_{eff} (BM)	Coupling constant $-J$ (cm^{-1})
L-glutamic acid	294	4.845	3.38	26.8
	80	6.834	2.10	
L-phenylalanine	294	4.933	3.42	25.0
	80	6.261	2.01	
L-histidine	294	5.399	3.57	22.7
	80	7.500	2.20	
S-benzyl-L-cysteine	294	4.514	3.27	28.0
	80	7.506	2.20	
L-arginine	294	4.182	3.14	28.0
	80	6.640	2.07	
L-threonine	294	4.072	3.40	25.0
	80	6.834	2.10	
L-hydroxyproline	294	4.123	3.12	30.2
	80	6.137	1.99	

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function of the L-amino acid residues is not involved in ligation to the irons and (b) coordination in these complexes occurs via the carboxyl function of the L-amino acid ligands and is not greatly affected by the presence of a particular side chain. This work also supports the conclusion[3] that the trimeric species $[Fe_3O]^{7+}$ present in the iron(III)-L-amino acid complexes may represent the building blocks of the ferritin iron core.

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