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Preparation and Properties of Iron(III)–L-Amino Acid Nitrates**

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Trinuclear oxobridged iron(III) carboxylates [1–4] containing the unit, $[Fe_3O]^{7+}$, have been known for some time. Recent work from our laboratory on the preparation and properties of the iron(III)–L-amino acid perchlorates [5–7] also containing the unit, $[Fe_3O]^{7+}$, emphasized the close similarity between the spectral and magnetic properties of these complexes and those of the ferritin iron core. More recently, iron(III)–L-amino acid tris(dihydrogen phosphito) nitrates have been prepared and their spectral and magnetic properties investigated [8] for a direct comparison of these properties with those of the ferritin iron core which also contains some phosphate [9]. In order to evaluate the properties of trinuclear iron(III)–L-amino acid nitrates containing phosphorus as model compounds for the ferritin iron core, it was deemed necessary to compare their spectral and magnetic properties directly with those of iron(III)–L-amino acid nitrates (Fig. 1) containing the trimeric iron(III) unit, $[Fe_3O]^{7+}$, but without the phosphorus containing ligand. Reasons for using iron(III) nitrate, and not iron(III) perchlorate, as the iron(III) providing reagent in the preparation of iron(III)–L-amino acid tris(dihydrogen phosphito) nitrates have been discussed in detail elsewhere [12]. The present paper describes the preparation and properties of trinuclear oxobridged iron(III)–L-amino acid nitrates derived from hydrophobic, aromatic, acidic, basic, hydroxy, and sulfur containing L-amino acids.

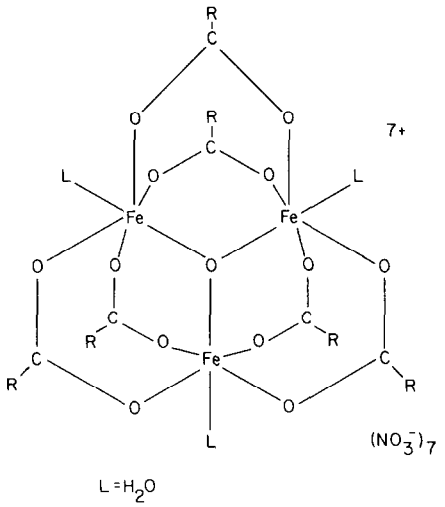

Fig. 1. Schematic representation of the molecular structure of the iron(III)–L-amino acid nitrates.

Experimental

The amino acid complexes derived from glycine, L-alanine, L-proline, L-valine, L-leucine, L-isoleucine, L-phenylalanine, L-histidine, L-serine, L-arginine, L-methionine, and L-aspartic acid were prepared by the general method similar to the one developed in our laboratory [5, 7] for the preparation of iron(III)–L-amino acid perchlorates. It consisted of mixing an aqueous solution of an L-amino acid with an aqueous solution of ferric nitrate nonahydrate, in a molar ratio of 2:1. Evaporation of the reaction mixture at room temperature gave, generally, a gummy solid which on maceration with nitromethane or acetonitrile yielded an orange or pink colored powder which was filtered and washed carefully with cold ethanol (absolute) and air dried. Caution needs to be exercised in a step involving maceration with nitromethane or acetonitrile; both these reagents form insoluble complexes (or addition compounds) with ferric nitrate (but not with ferric perchlorate), but washing the final product with cold ethanol removes any acetonitrile or nitromethane adduct present as an impurity in the desired complex, for the former is extremely soluble in ethanol.

All solution electronic spectra were obtained with a Cary 14 T spectrophotometer in methanolic solutions; solid state electronic spectra were obtained by mulling the complexes in nujol and mounting the mulls between quartz plates. Infrared spectra were obtained with a Beckman automatic recording, double-beam, optical null IR 10 infrared spectrophotometer. The spectra were taken using KBr pellets. Magnetic susceptibility measurements on solid samples were made using a Faraday balance consisting of a Cahn DTL-Electrobalance. Molecular weights were estimated from analytical data.

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

Amino Acid Complex	Element			
	C	H	N	Fe
Glycine – found	12.26	3.56	15.31	13.98
calcd for $[Fe_3O(glycine)_6(H_2O)_3](NO_3)_7$	12.80	3.20	16.20	14.92
L-alanine – found	18.14	3.56	14.42	12.26
calcd for $[Fe_3O(L\text{-}alanine)_6(H_2O)_3](NO_3)_7$	17.90	3.98	15.09	13.89
L-proline – found	25.64	4.40	13.82	11.37
calcd for $[Fe_3O(L\text{-}proline)_6(H_2O)_3](NO_3)_7$	26.44	4.40	13.36	12.29
L-valine – found	26.92	5.50	12.72	11.33
calcd for $[Fe_3O(L\text{-}valine)_6(H_2O)_3](NO_3)_7$	26.21	5.24	13.24	12.18
L-leucine – found	30.90	6.15	11.62	10.33
calcd for $[Fe_3O(L\text{-}leucine)_6(H_2O)_3](NO_3)_7$	29.64	5.76	12.48	11.48
L-isoleucine – found	30.72	6.14	11.84	10.57
calcd for $[Fe_3O(L\text{-}isoleucine)_6(H_2O)_3](NO_3)_7$	29.64	5.76	12.48	11.48
L-phenylalanine – found	9.86	38.04	4.80	10.39
calcd for $[Fe_3O(L\text{-}phenylalanine)_6(H_2O)_3](NO_3)_7$	10.02	38.70	5.01	10.87
L-histidine – found	25.71	3.90	20.24	10.12
calcd for $[Fe_3O(L\text{-}histidine)_6(H_2O)_3](NO_3)_7$	26.98	3.70	21.80	10.47
L-serine – found	15.25	3.94	11.01	10.60
calcd for $[Fe_3O(L\text{-}serine)_6(H_2O)_3](NO_3)_7$	15.14	3.78	10.94	11.76
L-arginine – found	17.49	4.53	14.33	12.97
calcd for $[Fe_3O(L\text{-}arginine)_6(H_2O)_3](NO_3)_7$	17.74	4.43	15.77	13.70
L-methionine – found	10.52	22.83	4.25	8.64
calcd for $[Fe_3O(L\text{-}methionine)_6(H_2O)_3](NO_3)_7$	10.73	23.03	4.41	8.67
L-aspartic acid – found	12.34	3.41	7.92	13.13
calcd for $[Fe_3O(L\text{-}aspartic\ acid)_6(H_2O)_3](NO_3)_7$	12.06	2.51	8.20	14.05

Results and Discussion

Analytical data for all the iron(III)–L-amino acid nitrates are presented in Table I. Observed values for elemental analyses differ from the calculated values for the postulated formulation of the trinuclear iron(III) complexes described in Table I. Similar deviations from calculated values for these elements in polynuclear iron(III) complexes have been reported by several investigators [3, 4, 7, 8, 10, 11]. Elemental analyses show correct amino acid/Fe ratios for the postulated formulations of the complexes.

TABLE II. Electronic Spectral Bands of Trinuclear Iron(III)–L-Amino Acid Nitrates in the Solid State (Nujol Mull).

Amino Acid Complex	Band Assignment, ν_{max}, cm^{-1}	
	Band I	Band II
glycine	10,204	16,233
L-alanine	10,416	16,129
L-proline	10,526	16,393
L-valine	10,638	16,260
L-leucine	10,416	16,393
L-isoleucine	10,752	16,181
L-phenylalanine	10,204	16,260
L-histidine	10,869	16,129
L-serine	10,309	16,207
L-arginine	10,638	16,129
L-methionine	10,638	16,181
L-aspartic acid	10,869	16,181

presented in Table III. The infrared spectra show broad and strong absorption in the region 3300–2800 cm^{-1} attributed to asymmetric and symmetric stretching modes [13–15] of NH_3^+ function in the L-amino acids present as ligands. The bands at *ca.* 1640 cm^{-1} and *ca.* 1440 cm^{-1} in the spectra of complexes are assigned to the asymmetric and symmetric carboxyl stretching modes [5, 7]. The $\Delta\nu$(COO), *i.e.* the difference between the asymmetric and symmetric carboxyl stretch is *ca.* 200 cm^{-1} and corresponds to the $\Delta\nu$(COO) observed in the spectra [5, 7] of the known iron(III)–L-amino acid perchlorates. Another characteristic feature of the infrared spectra of these complexes is the iron-oxygen stretch frequencies [5, 7, 16–18]. These are observed in the range 600–500 cm^{-1} and 460–360 cm^{-1}. The range of frequencies corresponds to the FeO stretch in the spectra [5, 7] of iron(III)–L-amino acid perchlorates and in the spectra [16–18] of known complexes of iron(III) octahedrally surrounded by oxygens. Three bands, in the spectra of all the complexes [12] in this study, at *ca.* 2400 cm^{-1}, *ca.* 1380 cm^{-1}, and *ca.* 830 cm^{-1} have been assigned to the coupled vibrational stretches $\nu_1 + \nu_3(NO_3)$ and NO stretching and NO bending modes of the NO_3 function [19–22]. The infrared spectral data coupled with information derived from analytical data show that L-amino acid ligands are present as zwitterions [*cf.* iron(III)–L-amino acid perchlorates (5, 7)].

TABLE III. Infrared Spectral[a] Bands of Iron(III)–L-Amino Acid Nitrates (Spectral Frequency Assignment, cm^{-1}).

L-Amino Acid Complex	ν_{as} (NH_3^+) and ν_{sym} (NH_3^+)	FeO[b]	FeO[b]	ν_{as}(COO)	ν_{sym} (COO)
glycine	3320–2900 b,s	600–520 b,w	390 b,w	1640 Shp,s	1465 Shp,s
L-alanine	3200–2800 b,s	590–540 b,s	410–390 b,s	1650 Shp,s	1440 Shp,s
L-proline		530–480 b,w	390 Shp,w	1650 Shp,s	1445 Shp,s
L-valine	3100–2890 b,s	450 Shp,w	390 Shp	1645 Shp,s	1450 Shp,s
L-leucine	3200–2800 b,s	480–430 b,w	290 Sh,w	1640 Shp,s	1450 Shp,s
L-isoleucine	3200–2850 b,s	600–520 b,w	410 Sh,w	1640 Shp,s	1650 Shp,s
L-phenylalanine	3200–2800 b,s	560 Shp,w	400 b,w	1640 Shp,s	1450 Shp,s
L-histidine	3200–2800 b,s	560–490 b,w	400 b,w	1630 Shp,s	1430 Shp,s
L-serine	3400–2900 b,s	600–520 b,w	420–380 b,w	1650 Sh,s	1450 Sh,s
L-arginine	3370–2900 b,s	600–500 b,w	460–380 b,w	1640 Sh,s	1440 Sh,s
L-methionine	3200–2800 b,s	590–530 b,w	460–380 b,w	1640 b,s	1440 Sh,s
L-aspartic acid	3300–2800 b,s	590–500 b,w	440–360 b,w	1640 Shp,s	1440 Shp,s

[a]Abbreviations: Shp, sharp; b, broad; Sh, shoulder; w, weak; m, medium; s, strong. [b]No attempt has been made to assign frequencies to asymmetric or symmetric Fe–O stretch.

The solid state electronic spectra (Table II) and the spectra of methanolic solution [12] show two absorption bands: band 1 in the range 10,000–11,000 cm^{-1} and band 2 in the range 16,000–16,500 cm^{-1} assigned to $^6A_1 \rightarrow {}^4T_1$ and $^6A_1 \rightarrow {}^4T_2$ transitions respectively. The spectral frequency range for the described transitions in the spectra of iron(III)–L-amino acid nitrates is in agreement with the values of similar transitions found in the spectra of known iron(III)–L-amino acid perchlorates [5, 7], iron(III)–L-amino acid tris(dihydrogen phosphito) nitrates [8], and iron(III)–carboxylates [4].

The infrared spectra of the iron(III)–L-amino acid nitrates containing the trimeric unit, $[Fe_3O]^{7+}$, are

The gram molar susceptibility per iron atom for nitrate complexes were found to be *ca.* 5000 × 10^{-6} csgu and the effective magnetic moment per

TABLE IV. Magnetic Susceptibilities and Magnetic Moments of Iron(III)–L-Amino Acid.[a]

Amino Acid Complex	Temperature (K)	$\chi_M \times 10^6$ (cgsu)	μ_{eff} (BM)	$-J$ (cm^{-1})
glycine	294	4.863	3.39	27.00
L-alanine	294	4,905	3.41	27.20
L-proline	294	5,218	3.51	22.70
L-valine	294	4,950	3.42	27.20
L-leucine	294	5,001	3.44	27.20
L-isoleucine	294	4,078	3.11	28.70
L-phenylalanine	294	5,076	3.47	26.99
L-histidine	294	4,022	3.09	27.08
L-serine	294	4,601	3.30	27.79
L-arginine	294	3,286	2.79	40.80
L-methionine	294	5,465	3.60	21.50
L-aspartic acid	294	4,863	3.40	27.20

[a]Symbols: χ_M, molar magnetic moment; μ_{eff}, magnetic susceptibility; J, coupling constant.

iron atom were found to be *ca.* 3.4 BM (Table IV). The methods used to calculate the exchange integral, $-J$, for these complexes are the same as discussed by Earnshaw *et al.* [23]; this value for the complexes in this work was found to be *ca.* 28 cm^{-1}. The magnetic data for the complexes in this work is in close agreement with that described for the similarly constituted known iron(III) complexes [3, 4, 5, 7] containing the unit, $[Fe_3O]^{7+}$. In the light of the fact that spectral and magnetic properties at room temperature of iron(III)–L-amino acid nitrates bear close similarity to those of the known iron(III) L-amino acid perchlorates [5, 7] and iron(III) carboxylates [3, 4], the nitrate complexes would be anticipated to be antifferomagnetic in character and it was deemed unnecessary to carry out the magnetic susceptibility measurements on the complexes at low temperature.

The study of the spectral and magnetic properties of the trinuclear oxobridged iron(III)–L-amino acid nitrates and the close similarity of these properties with those of the known trinuclear oxobridged iron(III)–L-amino acid perchlorates and trinuclear oxobridged iron(III)–carboxylates strengthens one view that the above physical properties of all the complexes are largely independent of the oxygen-containing ligands coordinated to the trimeric unit, $[Fe_3O]^{7+}$, and the nature of the counter-ion present in these complexes. This work also lends further support to our view [5, 7, 8] that iron(III) complexes containing the structural unit, $[Fe_3O]^{7+}$, remain strong contenders as models for the ferritin iron core.

References

1 B. N. Figgis and G. B. Robertson, *Nature, 205,* 694 (1965).
2 K. Amzenhofer and J. J. de Boer, *Rec. Trav. Chim., 88,* 286 (1969).
3 A. Bradshaw, B. N. Figgis and J. Lewis, *J. Chem. Soc. (A),* 1656 (1966).
4 G. J. Long, W. T. Robinson, W. P. Tappmeyer and D. L. Bridges, *J. Chem. Soc. Dalton,* 573 (1973).
5 W. F. Tucker, R. O. Asplund and S. L. Holt, *Arch. Biochem. Biophys.,* 166, 433 (1975).
6 E. M. Holt, S. L. Holt, W. F.Tucker, R. O. Asplund and K. J. Watson, *J. Am. Chem. Soc., 96,* 2621 (1974).
7 R. N. Puri, R. O. Asplund and S. L. Holt, in press.
8 R. N. Puri and R. O. Asplund, in press.
9 S. Granick, *J. Biol. Chem., 146,* 451 (1942).
10 C-H. S. Wu, G. R. Rossman, H. B. Gray, G. S. Hammond and H. J. Schugas, *Inorg. Chem., 11,* 990 (1972).
11 J. Carrerick, P. Thornton and B. W. Fitzsimmons, *J. Chem. Soc. Dalton,* 1420 (1976).
12 R. N. Puri, *Ph.D. Thesis,* The University of Wyoming, U.S.A., 1979.
13 I. M. Kotz and D. M. Gruen, *J. Phys. Chem., 52,* 961 (1948).
14 H. W. Thompson, D. L. Nicholson and L. N. Short, *Discussions Faraday Soc., 9,* 222 (1950).
15 K. Nakanishi, 'Infrared Absorption Spectroscopy', Holden-Day, Inc., San Francisco and Nakoda Company Limited, Tokyo, 1962, p. 39.
16 W. P. Griffith, *J. Chem. Soc. (A),* 2270 (1964).
17 J. Gujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys., 36,* 324, 331 (1962).
18 M. Mikami, I. Hakagawa and T. Shimanouchi, *Spectrochim. Acta, 23A,* 1037 (1967).
19 F. A. Miller and G. H. Wilkins, *Anal. Chem., 24,* 1253 (1952).
20 C. C. Addison and B. M. Gatehouse, *Chem. Ind.,* 464 (1955).
21 B. M. Gatehouse, S. E. Livingston and R. S. Nyholm, *J. Chem. Soc.,* 4222 (1957).
22 F. Vratny, *Appl. Spect., 13,* 59 (1959).
23 A. Earnshaw, B. N. Figgis and J. Lewis, *J. Chem. Soc. (A),* 1656 (1966).