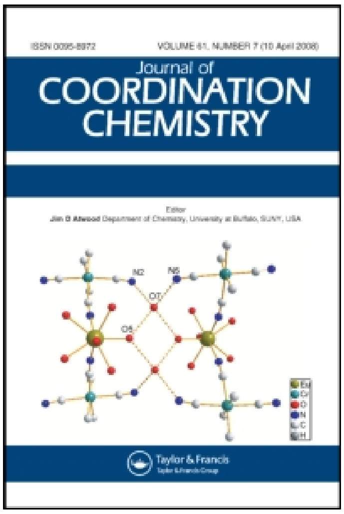

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CHARACTERIZATION OF DINUCLEAR DIALKOXOBRIDGED IRON(III)-L-PROLINE COMPLEXES AS THE REARRANGEMENT PRODUCTS OF TRINUCLEAR OXOBRIDGED IRON(III)-L-PROLINE COMPLEXES

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CHARACTERIZATION OF DINUCLEAR DIALKOXO-BRIDGED IRON(III)-L-PROLINE COMPLEXES AS THE REARRANGEMENT PRODUCTS OF TRINUCLEAR OXOBRIDGED IRON(III)-L-PROLINE COMPLEXES

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Dinuclear dimethoxolized iron(III)-L-proline complexes, obtained as a result of thermal, photolytic, and chemoreductive rearrangement of trinuclear oxobridged iron(III)-L-proline complexes, have been characterized by spectral and magnetic measurements. Under the conditions described, the rearrangement does not occur in other solvents nor when parallel complexes with other L-amino acids are used, including, surprisingly, L-hydroxyproline.

INTRODUCTION

Trinuclear oxobridged iron(III)-L-amino acid perchlorates derived from L-amino acids containing hydrophobic side chains have been studied earlier and their molecular[1] and crystal structure[2,3] determined in our laboratory. During the course of an extended investigation of trinuclear oxobridged iron(III)-L-amino acid complexes, we have observed that, of the trinuclear iron(III) complexes derived from glycine, L-proline, L-alanine, L-valine, L-leucine, and L-isoleucine[1] and L-hydroxyproline[4] examined, only the trinuclear oxobridged iron(III)-L-proline perchlorate [Figure 1(a)] and nitrate[5] [Figure 1(b)], in methanolic solutions were found to undergo thermal rearrangement; such rearrangements yielded light yellow products. The rearrangement products when refluxed in an aqueous solution reverted back to the original complexes. The trinuclear iron(III)-L-proline perchlorate could also be rearranged photolytically or chemoreductively to a deep yellow complex which was insoluble in water. Attempt to carry out the rearrangements in ethanol, n-propanol, iso-propanol, n-butanol, isobutanol, pentanol, and dioxane were unsuccessful. We were surprised to find that the complex derived from L-hydroxyproline did not undergo rearrangement by any of the methods described even in methanol. The

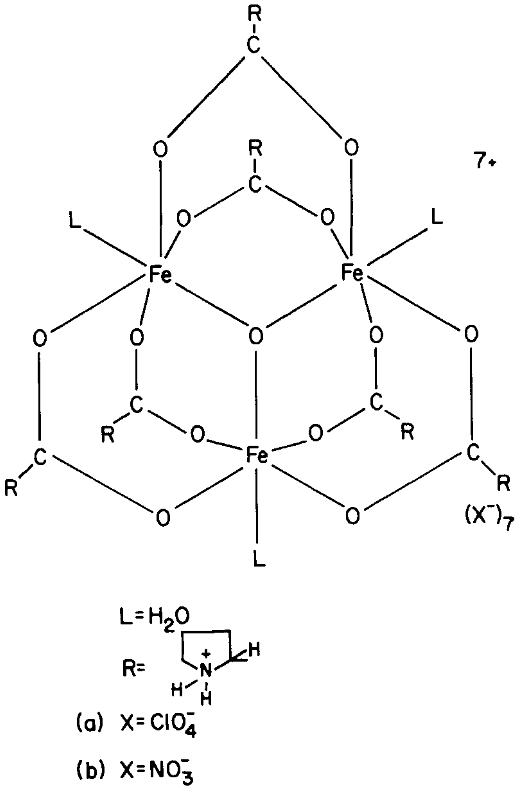

FIGURE 1 The structure of trinuclear iron(III) complexes: a) $[Fe_3O(L\text{-proline})_6(H_2O)_3](ClO_4)_7$ – structure established by X-ray analysis (Ref. 1); b) $[Fe_3O(L\text{-proline})_6(H_2O)_3](NO_3)_7$ – structure deduced from physical properties (Ref. 3).

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spectral and magnetic properties of the rearranged products suggest that their molecular structure [Figures 2(a) and (b)] consists of dinuclear dimethoxobridged iron(III) species. Due to the amorphous nature of the rearranged complexes, it was not possible to carry out X-ray diffraction studies on them. The electronic spectral and magnetic properties of the light yellow complex obtained by thermal rearrangement and the deep yellow product obtained by photolytic and chemoreductive rearrangements were nearly identical. A comparison of their infrared spectra showed considerable similarity; however the intensity of the Fe–O stretch frequencies in the spectra of the deep yellow complex were far more intense that those in the spectra of light yellow product. It is, therefore, reasonable to suggest that thermolytic, photolytic, and chemoreductive rearrangement yield the same kind of dinuclear dialkoxo iron(III) complex but the ones obtained by the latter two methods may be polymers.

EXPERIMENTAL

Photolysis of all complexes was attempted in an annular type photochemical reactor consisting of 16 irradiation lamps arranged in a 20 cm circle. The samples were either irradiated at ca. 3000 Å by means of G8T5 GE low pressure mercury arc lamps (General Electric Co., Inc.) or at 2537 Å using RPR model lamps (Southern New England Ultraviolet Co.). The samples were placed in a 29 x 2.8 cm quartz tube loosely plugged with glass wool at the mouth. All electronic spectra were recorded using a Cary 14R Spectrophotometer. Solid state spectra were obtained by mulling the complexes in nujol and mounting the mulls between quartz plates. Solution spectra were obtained in anhydrous methanol or in water. Infrared spectra from KBr pellets were obtained using a Beckman IR 10 infrared spectrophotometer. Magnetic susceptibility measurements on solid samples were made on a Faraday balance consisting of Cahn DTL-electrobalance. The magnet used was from Alpha Scientific Lab., model A 17500 m.

μ-Dimethoxo-bis[iron(III)-L-proline]perchlorate-(thermolytic)

Trinuclear iron(III)-L-proline perchlorate[1] (4.165 g) was refluxed in 250 ml anhydrous methanol for one hour. The reaction mixture was allowed to cool to room temperature and the product removed by filtration. The light yellow products (2.133 g, 84.7%) so obtained was washed with methanol and air-dried over night.

μ-Dimethoxo-bis[iron(III)-L-proline]perchlorate-(photolytic)

Trinuclear iron(III)-L-proline perchlorate (8.345 g) was dissolved in 200 ml anhydrous methanol. The methanolic solution was photolyzed in the photolytic reactor at 3000 Å for 7 days. The deep yellow precipitate (1.040 g, 20.6%) so formed was filtered, washed with methanol, and air dried over night. Photolysis of the trinuclear complex (7.5 g) in methanol, 450 ml, at 2583 Å yielded 2.143 g (47.3%) of the deep yellow precipitate.

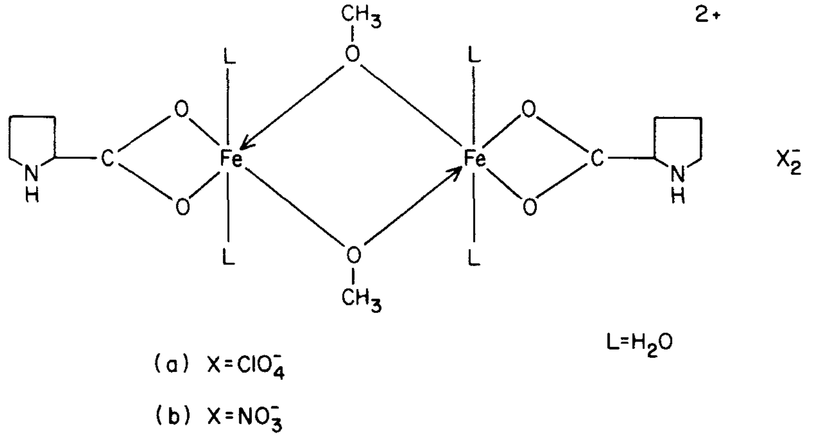


FIGURE 2 The structure of dinuclear iron(III) complexes: a) $[(\text{L-proline})\text{Fe}(\text{OCH}_3)(\text{H}_2\text{O})_2]_2(\text{ClO}_4)_2$; b) $[(\text{L-proline})\text{Fe}(\text{OCH}_3)(\text{H}_2\text{O})_2]_2(\text{NO}_3)_2$ – structure deduced from physical properties.

μ-Dimethoxo-bis[iron(III)-L-proline]perchlorate (chemoreductive)

Trinuclear iron(III)-L-proline perchlorate (2.086 g) was dissolved in 250 ml anhydrous methanol and freshly cut sodium (0.090 g, 1 equivalent/Fe atom of the complex) was added to the solution. The yellowish green solution on standing over night at room temperature yielded the dinuclear dimethoxo-iron(III)-L-proline perchlorate (0.674 g, 53.4%). It was filtered, washed with anhydrous methanol, and air dried over night.

μ-Dimethoxo-bis[iron(III)-L-proline]nitrate (thermolytic)

Trinuclear iron(III)-L-proline nitrate[5] (0.400 g) was dissolved in 50 ml anhydrous methanol and treated as was the perchlorate complex, except that reflux time was 2 hours. The complex (0.213 g, 97.7%) was washed with methanol and air dried over night.

TABLE I

Elemental analysis of dialkoxobridged dinuclear iron(III)-L-proline complexes (with postulated formulations).

Complex		Element				
		C	H	N	Cl	Fe
[(L-proline)Fe$(OCH_3)(H_2O)_2]_2(ClO_4)_2$[a]	Found	20.77	3.91	4.34	10.24	15.99
	calc.	21.40	4.50	4.16	10.50	16.60
[(L-proline)Fe$(OCH_3)(H_2O)_2]_2(ClO_4)_2{\cdot}2CH_3OH$[b]	Found	24.13	4.63	4.04	11.45	15.00
	calc.	22.80	5.10	3.80	9.60	15.20
[(L-proline)Fe$(OCH_3)(H_2O)_2]_2(ClO_4)_2{\cdot}2CH_3OH$[c]	Found	23.50	4.84	3.90	11.20	15.50
	calc.	22.80	5.10	3.80	9.60	15.20
[L-proline)Fe$(OCH_3)(H_2O)_2]_2(ClO_4)_2{\cdot}2CH_3OH$[d]	Found	22.70	4.91	4.00	10.14	15.39
	calc.	22.80	5.10	3.80	9.60	16.60
[(L-proline)Fe$(OCH_3)(H_2O)_2]_2(NO_3)_2$	Found	24.00	4.89	9.75		19.67
	calc.	24.29	5.02	9.37		18.60

[a] Prepared by thermal treatment.
[b] Prepared by photolysis at 3000 Å.
[c] Prepared by photolysis at 2537 Å.
[d] Prepared by treatment with NaOMe.

Rearrangement of the μ-dimethoxo-bis[iron(III)-L-proline]perchlorate and nitrate to the trinuclear iron(III)-L-proline perchlorate and nitrate

μ-Dimethoxo-bis[iron(III)-L-proline]perchlorate (1.000 g) was refluxed in water for one-half hour. The resulting solution was cooled and allowed to evaporate at room temperature. The trinuclear iron(III)-L-proline perchlorate (0.554 g, 33.6%) obtained as glassy solid was filtered and air dried. Its properties were identical with those of a known sample. μ-Dimethoxo-bis[iron(III)-L-proline]nitrate (0.075 g) under identical work up yielded 0.030 g (28.3%) of the trinuclear iron(III) complex.

The percentage yields of the rearrangement products were estimated assuming two molecules of the trinuclear iron(III) complex yield three molecules of the dinuclear iron(III) complex on rearrangement. Elemental analyses were obtained from commercial sources and each value shown in Table I represents the mean of at least two separate analyses. Molecular weights were estimated from analytical data.

RESULTS AND DISCUSSION

All the complexes described have been subjected to elemental analysis as shown in Table I. Elemental analyses show correct amino acid/Fe ratios for the postulated formulations of the dinuclear dimethoxobridged iron(III)-L-proline complexes. The experimentally determined analytical values for the postulated formulations of the dinuclear iron(III)-L-proline complexes differ from the calculated values in the range 1–4%; similar deviations have been frequently encountered in analysis of polynuclear oxobridged iron(III) complexes by ourselves and others.[1,6,7,8] The elemental analyses together with the infrared spectral data to be presented below suggest that the L-amino acid ligand in these complexes is not present as the

TABLE II
Electronic spectral bands of dialkoxobridged dinuclear iron(III)-L-proline complexes in nujol (Mull).

	ν_{max}·cm^{-1}	
	Band 1	Band 2
[(L-proline)Fe(OCH_3)(H_2O)$_2$]$_2$(ClO_4)$_2$[a]	10,638	13,513
[(L-proline)Fe(OCH_3)(H_2O)$_2$]$_2$(ClO_4)$_2$·2CH_3OH[b]	10,638	13,513
[(L-proline)Fe(OCH_3)H_2O)$_2$]$_2$(ClO_4)$_2$·2CH_3OH[c]	10,638	13,513
[(L-proline)Fe(OCH_3)(H_2O)$_2$]$_2$(ClO_4)$_2$·2CH_3OH[d]	10,638	13,513
[(L-proline)Fe(OCH_3)(H_2O)$_2$]$_2$(NO_3)$_2$[e]	10,416	13,888

[a] Prepared by thermal treatment.
[b] Prepared by photolysis at 3000 Å.
[c] Prepared by photolysis at 2537 Å.
[d] Prepared by treatment with NaOMe.
[e] Reference 5.

Zwitterion and the nitrogen atom of L-proline residue carries no positive charge.

ELECTRONIC SPECTRA

The solid state electronic spectra of the dinuclear dimethoxobridged iron(III)-L-proline complexes have been recorded and are presented in Table II. The spectra in the near-ir region show two bands–band 1 at ca. 10,600 cm^{-1} and band 2 at ca. 13,500 cm^{-1}; the intensity of the bands is very low.[9] These absorption spectra compare favorably with those of known dinuclear dialkoxobridged iron(III) complexes[6] (Table III). Following Piper *et al.*[10] and Wu *et al.*,[6] the two bands mentioned may be assigned to spin-forbidden d–d transitions $6A_1 \rightarrow 4T_1$ and $6A_2 \rightarrow 4T_2$ respectively. This band assignment is not, however, firm in the absence of X-ray diffraction data concerning the symmetry properties of the complexes in question. There is one evident difference between the solid state spectra of the dinuclear dimethoxobridged iron-(III)-L-proline complexes (Table III) and the trinuclear oxobridged iron(III)-L-proline complexes;[1,4] the higher energy band in the former complex is located at ca. 13,500 while in the latter it is found at ca. 16,000 cm^{-1}. It is also instructive to compare the electronic spectra of the complexes in question with those of the dinuclear oxobridged complexes[25] containing the Fe_2O^{4+} unit; the spectra in the near-ir region show two ligand field bands at ca. 11,300 and 18,400 cm^{-1} corresponding to $6A_1 \rightarrow 4T_1$ and $6A_1 \rightarrow 4T_2$ transitions respectively, and it is the latter that is noticeably different from those of the previously mentioned trinuclear oxobridged and dinuclear dialkoxobridged iron(III) complexes. It is, therefore, clear that the frequencies of the two electronic bands in the near-ir region, corresponding to ligand field transitions $6A_1 \rightarrow 4T_1$ and $6A_1 \rightarrow 4T_2$, in the spectra of polynuclear oxobridged iron(III) complexes are characteristic of a particular geometry of the iron–oxygen bridge and hence can be used to distinguish among these. Furthermore, in the spectra of the dinuclear dialkoxobridged iron(III) complexes the two electronic bands described are relatively unaffected by the nature of nonbridging oxygen containing ligands, *e.g.*, L-amino acid, acac, DPM coordinated to iron(III) atoms. The electronic spectra of L-proline complexes, in this paper, in aqueous solution are shown in Table IV. Both the absorption

TABLE III
Electronic spectral bands of known dialkoxobridged dinuclear iron(III) complexes.

		Spectral Frequency Assignment, ν_{max}·cm^{-1}	
Complex	Conditions	$^6A_1 \rightarrow {}^4T_1$	$^6A_1 \rightarrow {}^4T_2$
[$(DPM)_2Fe(OCH_3)$]$_2$[a]	Cyclohexane soln. room temp.	10,700	14,100
[$(acac)_2Fe(O_2C_2H_5)$]$_2$[b]	Cyclohexane soln. room temp.	10,100	13,800

[a] DPM, 2,2,6,6-tetramethylheptane-3,5-dione.
[b] acac, acetylacetone.

bands are shifted to higher energy regions probably due to greater splitting of t_{2g} and e_g levels by the increased polarity of the solvent. The electronic spectral data of corresponding trinuclear oxobridged iron(III)-L-proline complex in aqueous medium is also presented in Table IV for comparison purposes: the higher energy band again distinguishes between the two different types of oxobridged iron(III) complexes.

TABLE IV
Electronic spectral bands of trinuclear oxobridged and dinuclear dialkoxobridged iron(III)-L-proline complexes in aqueous solution.

	ν_{max}, cm^{-1}	
	Band 1	Band 2
$[(L\text{-proline})Fe(OCH_3(H_2O)_2]_2(ClO_4)_2$[a]	*11,111*	16,129
$[(L\text{-proline}(Fe(OCH_3)(H_2O)_2]_2(NO_3)_2$	11,363	16,129
$[Fe_3O(L\text{-proline})_6(H_2O)_3](ClO_4)_7$[b]	11,100	20,833
$[Fe_3O(L\text{-proline})_6(H_2O)_3](NO_3)_7$[c]	11,290	21,276

[a] Prepared by thermal treatment.
[b] Reference 4.
[c] Reference 5.

INFRARED SPECTRA

The infrared spectra of the dinuclear dialkoxobridged iron(III)-L-proline complexes are presented in Tables V, VI, and VII. There are several characteristic features in the spectra of these complexes which are different from those of the spectra of corresponding trinuclear oxobridged iron(III)-L-amino acid complexes.[1,4,5] The N—H stretching mode is observed at ca. 3000 cm^{-1}. The frequency of the stretching mode of a secondary amino function may be attributed to

TABLE V
Infrared spectral[a] bands of dialkoxobridged dinuclear iron(III)-L-proline complexes.

	Frequency assignment, cm^{-1}				
Complex	$\nu_{as}(COO)$	$\nu_{sy}(COO)$	$\Delta\nu(COO)$	$\nu(FeO)$[b]	$\nu(FeO)$[b]
$[(L\text{-proline})Fe(OCH_3)(H_2O)]_2(ClO_4)_2$[c]	$1590^{b,s}$	$1430^{shp,s}$	160	$500\text{–}420^{b,w}$	$400\text{–}350^{b}$
$[(L\text{-proline})Fe(OCH_3)(H_2O)]_2(ClO_4)_2 \cdot 2CH_3OH$[5]	$1600^{b,s}$	$1460^{shp,s}$	140	$500\text{–}410^{b,m}$	$400\text{–}360^{b}$
$[(L\text{-proline})Fe(OCH_3)(H_2O)]_2(NO_3)_2$[e]	$1570^{b,s}$	$1439^{shp,s}$	151	$500\text{–}420^{b,m}$	$400\text{–}350^{b}$
$[FeO(L\text{-proline})_6(H_2O)_3](ClO_4)_7$[f]	$1628^{b,s}$	$1438^{shp,s}$	190	570	—

[a] Abbreviations: shp, sharp; b, broad; sh, shoulder; w, weak; m, medium; s, strong; as, asymmetric; sy, symmetric.
[b] Assignment to symmetric and asymmetric stretch not made.
[c] Prepared by thermal treatment.
[d] Prepared by photolysis at 3000 Å (the preparation by photolysis at 2537 Å and by $NaOCH_3$ treatment showed the same spectrum within experimental error).
[e] Reference 5.
[f] Tri-iron complex included for comparison.

TABLE VI
Infrared spectral[a] bands of dialkoxobridged dinuclear iron(III)-L-proline complexes.

	Frequency assignment, cm^{-1}			
	$\nu_{(N—H)}$	$\nu_{(C—O,OCH_3)}$	$\nu_{3(ClO_4)}$	$\nu_{4(ClO_4)}$
$[L\text{-proline})Fe(OCH_3)(H_2O)_2]_2(ClO_4)_2$[b]	$3100\text{–}2900^{b,s}$	$1030^{b,m}$	$1140\text{–}1080^{b,s}$	$620^{shp,m}$
$[(L\text{-proline})Fe(OCH_3)(H_2O)_2]_2(ClO_4)_2 \cdot 2CH_3OH$[c]	$3000\text{–}2880^{b,s}$	$1035^{shp,s}$	$1130\text{–}1050^{b,s}$	$620^{shp,m}$
$[(L\text{-proline})Fe(OCH_3))(H_2O)_2]_2(NO_3)_2$	$3000\text{–}2860^{b,s}$	$1030^{shp,s}$	—	—
$[Fe_3O(L\text{-proline})_6(H_2O)_3](ClO_4)_7$[d]	$3260\text{–}2960^{b,s}$	—	$1130\text{–}1010^{b,s}$	$620^{shp,m}$

[a] Abbreviations: shp, sharp; b, broad; sh, shoulder; w, weak; s, strong; m, medium; as, asymmetric; sy, symmetric.
[b] Prepared by thermal treatment.
[c] Prepared by photolysis at 3000 Å (the preparations by photolysis as 2537 Å and by $NaOCH_3$ treatment showed the same spectrum within experimental error).
[d] Tri-iron complex included for comparison.

the hydrogen bonding of the N—H group and the electron withdrawing effect of the carboxyl group in the alpha position of the proline ring (Cf. NHCO group) and its subsequent ligation to the iron atom of the complex. The fact that the secondary amino stretching mode appears at ca. 3000 cm^{-1} and not at 2700 cm^{-1}, strongly supports[11] the contention that the secondary amino function of L-proline in these complexes is not present as NH$_2^+$. This is also borne out by the elemental analyses of the complexes, which would otherwise require a different charge balance. The dinuclear complexes obtained by photolytic and chemoreductive rearrangement show broad and strong absorption (Table VII) at ca. 3200 cm^{-1}. This is attributed to methanol molecules of crystallization[12] present in these complexes. These methanol molecules are probably hydrogen bonded to perchlorate ions which in turn are hydrogen bonded to the NH group of the proline residues[3] in these complexes. A very important spectral frequency in the infrared spectra of the dimeric iron(III)-L-proline complexes is located at ca. 1030 cm^{-1}; this corresponds to the C—O stretching mode in alcohols[13] typically found at ca. 1050 cm^{-1}. In similarly constituted dinuclear dialkoxobridged iron(III) complexes, *e.g.*, [(DPM)$_2$-Fe(OCH)$_3$]$_2$ and [(N—piCO)$_2$Fe(OCH$_3$)]$_2$, Wu *et al.*,[6] have assigned the absorption band at ca. 1030 cm^{-1} to the bridging methoxo group between the two irons. Barraclough *et al.*,[14] assigned two frequencies at ca. 1030 and 1070 cm^{-1} to C—O stretch in the infrared spectra of the complexes Ti(OC$_2$H$_5$)$_5$, and Nb(OC$_2$H$_5$)$_5$. Since all the complexes under consideration either with or without methanol of crystallization exhibit a frequency at ca. 1030 cm^{-1}, it is, therefore, concluded that they contain bridging methoxo groups. Furthermore, the dinuclear dihydroxobridged iron(III) complexes, *e.g.*, [Dipic(H$_2$O)FeOH] and [Chel(H$_2$O)FeOH]$_2$·4H$_2$O have been extensively investigated by Thick *et al.*,[15] and Schugar *et at.*;[16] these complexes contain a frequency at ca. 900 cm^{-1} attributed to the deformation mode of the bridging OH function. Further, ferric dimers, *e.g.*, enH$_2$[HEDTAFe$_2$)O]·6H$_2$O containing Fe—O—Fe bridge have been described;[17] these complexes each exhibit a band at 858 cm^{-1} characteristic of the oxobridge present in their molecular structure. From the foregoing discussion it is highly probable that in the dinuclear dimethoxobridged iron(III)-L-proline complexes it is a methoxo group that bridges the irons and not a hydroxo or oxo function. One of the most noticeable features in the infrared spectra of the dimeric iron(III)-L-proline complexes is the location of the frequencies corresponding to the asymmetric and symmetric carboxyl stretch modes that appear at ca. 1580 and 1440 cm^{-1} respectively. The $\Delta\nu$ between these two stretches (Table V) is in the range 140–160 cm^{-1} in all the complexes examined. Although the frequency of the symmetric stretch of the carboxyl function of the complexes under consideration is shifted to a higher energy region by ca. 40 cm^{-1}, the asymmetric stretch occurs at the frequency found in the spectra[18] of L-amino acids. It, therefore, appears that in the dinuclear dimethoxobridged iron(III)-L-proline complexes, the carboxyl function of L-proline residue is coordinated to iron(III) either in a monodentate fashion or in a highly unsymmetrical bidentate fashion.[19] The molecular structure, Figure II, assigned to the dinuclear dimethoxobridged iron(III)-L-proline complexes is, therefore, tentative. The $\Delta\nu$ between the asymmetric and symmetric stretching modes of the carboxyl function in the trinuclear oxobridged

TABLE VII

Infrared spectral[a] bands of dialkoxobridged dinuclear iron(III)-L-proline complexes.

	Spectral Frequency Assignment, cm^{-1}	
	$\nu_{asym}(H_2O)$ and $\nu_{sym}(H_2O)$	ν(OH, alcohol)
[(L-proline)Fe(OCH$_3$)(H$_2$O)$_2$]$_2$(ClO$_4$)$_2$[b]	3600–3300^{b,s}	
[(L-proline)Fe(OCH$_3$)(H$_2$O)$_2$]$_2$(ClO$_4$)$_2$·2MeOH[c]	3600–3300^{b,s}	3280–3200^{sh,s}
[(L-proline)Fe(OCH$_3$)(H$_2$O)$_2$]$_2$(ClO$_4$)$_2$·2MeOH[d]	3600–3340^{b,s}	3260–3060^{b,s}
[(L-proline)Fe(OCH$_3$)(H$_2$O)$_2$]$_2$(ClO$_4$)$_2$·2MeOH[e]	3600–3320^{b,s}	3200–3100^{b,s}
[(L-proline)Fe(OCH$_3$)(H$_2$O)$_2$]$_2$(NO$_3$)$_2$	3600–3100^{b,s}	

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

[b] Prepared by thermal treatment.

[c] Prepared by photolysis at 3000 Å.

[d] Prepared by photolysis at 2537 Å.

[e] Prepared by treatment with NaOMe.

TABLE VIII
Magnetic susceptibilities and magnetic moments of dialkoxobridged dinuclear iron(III)-L-proline complexes.

Complex	Temperature (°K)	$\chi_m \times 10^6$ (cgms)	μ_{eff} (BM)	$-J$ (cm^{-1})
$[(\text{L-proline})Fe(OCH_3)(H_2O)_2]_2(ClO_4)_2$[a]	294	7,966	4.34	8.50
$[(\text{L-proline})Fe(OCH_3)(H_2O)_2]_2(ClO_4)_2 \cdot 2MeOH$[b]	294	7,700	4.27	9.28
$[(\text{L-proline})Fe(OCH_3)(H_2O)_2]_2(ClO_4)_2 \cdot 2MeOH$[c]	294	7,650	4.26	9.37
$[(\text{L-proline})Fe(OCH_3)(H_2O)_2]_2(ClO_4)_2 \cdot 2MeOH$[d]	294	7,650	4.26	9.37
$[(\text{L-proline})Fe(OCH_3)(H_2O)_2]_2(NO_3)_2$	294	8,903	4.54	7.50

[a] Prepared by thermal treatment.
[b] Prepared by photolysis at 3000 Å.
[c] Prepared by photolysis at 2537 Å.
[d] Prepared by treatment with NaOMe.

iron(III) complexes[1,4,5] is of the order of 200 cm^{-1}. Thus, it is also clear that $\Delta\nu$(COO—the difference between the stretch frequencies of the asymmetric and symmetric modes of the carboxyl function—is a diagnostic feature that distinguishes between the trinuclear oxobridged iron(III)-L-proline and the dinuclear dimethoxobridged iron(III)-L-proline complexes. The infrared spectra of the dinuclear complexes in this work contain characteristic frequencies in the range 500–400 cm^{-1}; this is one of the two Fe—O stretching modes, and the corresponding Fe—O stretching mode in the spectra of trinuclear oxobridged iron(III)-L-amino acid complexes, including the one derived from L-proline, has been found in the range 575–540 cm^{-1}. The nature of the infrared frequencies corresponding to Fe—O linkage in iron(III)-L-amino acid complexes has been dealt with in detail elsewhere.[4,9] The absorption bands in the range 1140–1050 cm^{-1} and at 620 cm^{-1} in the spectra of L-proline complexes in this work are attributed to ν_3 and ν_4 modes of the perchlorate anion;[20] the bands at ca. 2400, 1380, and 830 cm^{-1} correspond to the combination mode $\nu_1 + \nu_2(NO_3)$, the asymmetric N—O stretching, and N—O bending modes, respectively, of the nitrate function.[21]

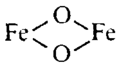
MAGNETIC PROPERTIES

The magnetic susceptibility per iron atom and magnetic moment per iron atom of the dimeric iron(III)-L-proline complexes at 295°K are presented in Table VIII. Values of the exchange integral, $-J$, were calculated using an approximation by the method of Earnshaw *et al.*[22] In calculating the exchange integral, $-J$, it was assumed that Fe—O—Fe angle in the complexes in question is of the order of 90°. The exchange integral appropriate to such a system could, then, simply be obtained by multiplying 1/2 the values for a linear chain of three members. For all the L-proline complexes examined, the value of μ_{eff} was found to be 4.3 BM at 295°K and the corresponding $-J$ value was found to be ca. 9 cm^{-1}; it compares well with those of the similarly constituted known dinuclear dimethoxobridged iron(III)[6] and dinuclear dihydroxobridged iron(III) complexes.[15] Table IX provides a comparison of the $-J$ values for the various polynuclear iron(III) complexes and it brings out a molecular structural resemblance of the dinuclear dimethoxobridged iron(III)-L-proline complexes with the known dinuclear dihydroxobridged iron(III) complexes—containing the basic building units

TABLE IX
Exchange integral values for various polynuclear iron(III) complexes.

Complex	Basic Structural Unit	$-J$(cm^{-1})	Reference
$[(\text{L-proline})Fe(OCH_3)(H_2O)_2]_2(ClO_4)_2$	$Fe_2(OCH_3)_2{}^{4+}$	8.50	This work
$[(\text{L-proline})Fe(OCH_3)(H_2O)_2]_2(NO_3)_2$	$Fe_2(OCH_3)_2{}^{4+}$	7.50	This work
$[(DPM)_2Fe(OCH_3)]_2$	$Fe_2(OCH_3)_2{}^{4+}$	ca. 8.0	6
$[(\text{N-PiCO})_2Fe(OCH_3)]_2$	$Fe_2(OCH_3)_2{}^{4+}$	ca. 10.0	6
$[(Dipic)(H_2O)FeOH]_2$	$Fe_2(OH_2{}^{4+}$	11.40	15
$[(Chel)(H_2O)FeOH]_2$	$Fe(OH)_2{}^{4+}$	7.30	15
$[(\text{L-proline})_6Fe_3O(H_2O)_3](ClO_4)_7$	Fe_3O^{7+}	28.0	1
$[(\text{L-proline})_6Fe_3O(H_2O)_3](NO_3)_7$	Fe_3O^{7+}	22.70	5, 9
$EnH_2[FeHEDTA)_2O]$	Fe_2O^{4+}	95	25
$Na_4[(FeEDTA)_2O] \cdot 12H_2O$	Fe_2O^{4+}	99	25

$Fe_2(OR)_2^{2+}$ and $Fe_2(OH)_2^{2+}$ respectively. A value of ca. 4.3 BM for the magnetic moment per iron atom at room temperature with a corresponding value of ca. 9 cm^{-1} for the exchange integral observed for almost all the dimeric iron(III)-L-proline complexes, suggests that some spin coupling occurs through orbital overlap via the bridging oxygen of the unit $Fe_2(OR)_2^{4+}$ as postulated in the superexchange mechanism propounded (discussed) by Ginsberg[23] and Murray.[24] Data presented in Table I bring out one important fact: the value of exchange integral, $-J$, although capable of distinguishing trimeric iron(III) species, Fe_3O^{7+}, dimeric iron(III) species $Fe_2(OR)_2^{4+}$ or $Fe_2(OH)_2^{4+}$ and the dimeric iron(III) species Fe_2O^{4+}, cannot distinguish between complexes containing the $Fe(OR)_2^{4-}$ unit from those containing the $Fe_2(OH)_2^{4+}$ unit as the building blocks of their gross molecular structure. We concur with Wu *et al.*,[6] that the magnetic properties and the antiferromagnetism exhibited by the complexes containing either the $Fe_2(OR)_2^{4-}$ or $Fe_2(OH)_2^{4+}$ species is basically due to the presence of the unit



in the molecular structure and the exact value of the exchange integral, $-J$, is largely dependent on the Fe—O—Fe angle and much less so on the bridging oxygen function.

In summary, the complexes described in this paper have been shown to contain the dinuclear dimethoxo-bridged iron(III)$_3$, $Fe_2(OCH_3)_2^{4+}$, unit based on the evidence obtained from analytical, electronic and infrared spectral, and magnetic measurements. Diagnostic properties are: (1) the higher energy band, band 2, in the near-ir region of the electronic spectrum, at ca. 14,000 cm^{-1}; (2) in the ir spectrum, the carboxyl stretching bands at ca. 1600 and 1440 cm^{-1}, the secondary amino stretching band at ca. 3000 cm^{-1}, C—O stretch of the methoxo function bridging the irons at ca. 1030 cm^{-1}, and the Fe—O stretching bands at 500–410 cm^{-1} and 400–350 cm^{-1}; (3) the magnetic susceptibility of ca. 4.3 BM with a $-J$ value of ca. 9 cm^{-1}. They appear to be weakly antiferromagnetic in character. It is interesting to point out, in passing, that spectral and magnetic properties of dinuclear dialkoxobridged iron(III)-L-proline complexes are different from those of the corresponding trinuclear oxobridged iron(III)-L-proline complexes which remain the strong contenders as model compounds[1] for the ferritin iron core.

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