The CD Spectra of Tri-μ_3-Oxo-Triaquohexakis(L-Amino Acid)triiron(III) Perchlorates

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Circular dichroic spectra of tri-μ3-oxo triaquo-hexakis(L-amino acid)triiron(III) complexes, containing the [Fe3O]7+ unit, proposed as models for ferritin iron core, are described. The circular dichromism of these iron(III)–L-amino acid complexes is mainly due to the interaction of the charge transfer manifold with the asymmetric carbon atom of L-amino acids. Although it is possible to correlate the optical extrema with the electronic spectra of the complexes, it is not possible to correlate the sign of the extrema in the CD spectra of the complexes with specific features of their molecular structure. Extrema for complexes derived from five L-amino acids with aliphatic R group occur at the same wavelengths in each case: 218(+), 245(−), 267(+), 311(+), 345(+), 378(−), 475(+), 538(+), and 620(+). Complexes using D-amino acids exhibit spectra which are the antipodes of these. Maximum spectra are observed when perchlorate is used as the counterion.

Fig. 1. Schematic representation of the molecular structure of $[Fe_3O(L\text{-amino acid})_6(H_2O)_3](ClO_4)_7$ complexes as deduced from spectral and magnetic properties [Ref. 1, 2, 4] and X-ray diffraction [Ref. 5].

Introduction

Tri-μ_3-oxo-triaquohexakis(L-amino acid)triiron(III) perchlorates, Fig. 1, and similarly constituted nitrates (more commonly known as iron(III)–L-amino acid perchlorates and nitrates) containing the trimeric $[Fe_3O]^{7+}$ unit have been proposed as models for the ferritin iron core. Their structures have been established by detailed study of their spectral and magnetic properties [1–3] and X-ray diffraction patterns [4, 5]. The cation with the general formula $[Fe_3O(L\text{-amino acid})_6(H_2O)_3]^{7+}$ has crystallographic point symmetry 3, the iron atoms forming an equilateral triangle of side 3.29 Å, with the central oxygen atom on the three-fold axis. Each amino acid ligand is close to being coplanar with the irons it bridges (maximum deviation 0.50 Å). Coordination of each iron is octahedral and the L-amino acid
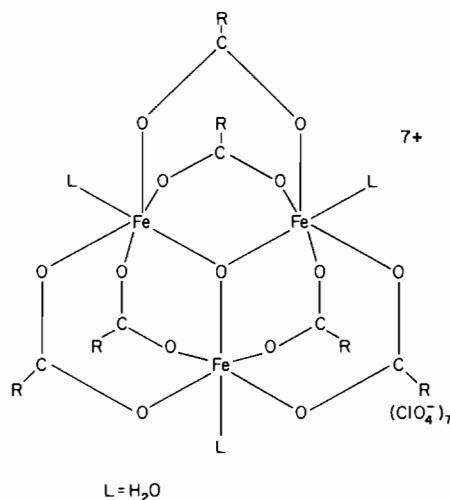
ligands are present as zwitterions. The electronic spectra of iron(III)–L-amino acid perchlorates have been well characterized by the authors and described in considerable detail elsewhere [1–3]. The overall structure of the complexes in this work is highly symmetrical with regard to complex formation. This is in marked contrast to the tetrahedral and octahedral complexes formed by other transition metal ions with α-amino acids which offer a rich variety of inherent asymmetries [6]. Although the CD spectra of L-amino acid complexes derived from Co(III) [7], Cu(II) [8], Ni(II) [9], and Cr(III) [10] have been described in some detail, there is a paucity of literature on the dichroic spectra of iron(III) complexes with α-amino acids. Some attempts have been made to characterize the CD spectra of iron(II) complexes [10, 11], but not with α-amino acid ligands. This paper describes the first report on the CD spectra of polynuclear high spin iron(III) complexes. The CD spectra of iron(III)–L-amino acid complexes in this work correlate well with absorption bands in their

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electronic spectra. However, the relationship between the sign of the extrema in their dichroic spectra and the molecular structure is less well understood. The chirooptical properties of the high spin iron(III) complexes in this work arise largely from the asymmetric carbon atoms and the perturbation these exert on neighbouring chromophores and the d—d transitions in the irons. In this paper, data on the CD spectra of tri-μ_3-oxo triaquohexakis(L-amino acid)triiron(III) perchlorates derived from five L-amino acids containing aliphatic R groups are presented which support this view. For the sake of simplicity, these complexes have been identified with the name iron(III)—L-amino acid perchlorates throughout this paper.

Experimental

Crystalline complexes having the general formula [Fe$_3$O(L-amino acid)$_6$(H$_2$O)$_3$](ClO$_4$)$_7$·xH$_2$O, derived from L-alanine, L-proline, L-valine, L-leucine, L-isoleucine were prepared as previously described [1, 12]. Solutions of these complexes in absolute methanol were prepared volumetrically. Solutions showing identical properties could also be prepared by dissolving stoichiometric amounts of optically active amino acids and Fe(ClO$_4$)$_3$·6H$_2$O in absolute methanol. Complexes containing anions other than perchlorate were prepared by dissolving the appropriate iron salt in methanol along with the required stoichiometric amount of the amino acid. CD spectra were obtained by means of a Durrum-Jasco J20 spectrophotometer. Solution concentrations ranged from 0.001 M to 0.004 M which was the range over which a useful $\Delta\epsilon/\epsilon$ ratio could be obtained. Spectra were routinely taken from 195–630 nm. Light paths were 195–320 nm, 10^{-4} m; 320–420 nm, 10^{-3} m;

420–620 nm, 10^{-2} m. All observed rotations are reported as molar degrees ellipticity (θ_m) and described in Table I.

The single crystal and methanolic solution electronic spectra were recorded as previously described [1, 4] using a Cary 14R spectrophotometer. The electronic spectral data are summarized in Table II.

Results and Discussion

The interpretation of the data obtained depends upon the assumption that the complexes have the same structure in solution as they do in crystalline state. That this is very probably true is supported by three lines of evidence; for these complexes, the solution electronic spectra, the solution magnetic susceptibility, and the Mössbauer spectra are quantitatively very nearly the same as are these properties for crystalline state [13]. Therefore, the assumption that the structure of the complexes in solution retains all the necessary features of their molecular structure in the crystalline state is valid for the interpretation of the CD spectra of these complexes in solution and its relationship to the electronic spectra in the crystalline or solution state.

The observed electronic spectra of trinuclear oxo-bridged iron(III) perchlorates consist of essentially four bands (Table II): band I at ca. 200–425 nm, band II at ca. 475 nm, band III at ca. 620 nm, and band IV at 909 nm. Band I is a very high intensity band, band II is a low intensity band, and bands III and IV are of very low intensity. The CD spectra of the complexes in this work exhibit extrema at corresponding wavelengths except for the fact that CD spectra in the wavelength region 900–1000 nm could not be recorded on the instrument available to

TABLE I. Calculated Molar Ellipticities of the Extrema from the Circular Dichroic Spectra of Iron(III)–Amino Acid Perchlorates.

Wave Length (nm)	Sign of Extrema	$[\theta]_m^c$ Values Complexes of Amino Acid				
		Alanine	Proline	Valine	Leucine	Isoleucine
218	+	9.0×10^3	8.4×10^3	1.8×10^4	3.0×10^4	1.9×10^4
245	–	−6210	−2090	−1110	−4960	−2110
267	+	a	0	1650	9300	738
311	+	a	355	710	4960	0 b
345	+	a	435	1180	9960	494
378	–	−222	−278	−2050	−1160	−2370
459	–	−17.0	−19.9	−148	−241	−37.2
475	+	30.0	d	40.1	35.0	34.1
538	+	6.11	d	27.0	17.2	a
620	+	0.32	d	4.10	7.02	a

aNot observable at the limit of $\Delta\epsilon/\epsilon \approx 10^{-6}$ (cf. instrument used to scan the CD spectra).   bExtremum peak at $\theta = 0$.   cFor extrema 218–475, C = 4.0×10^{-3} M, for extrema 538–620, C = 1.0×10^{-1} M.   dComplex only partially soluble at this concentration.

TABLE II. Electronic Spectral Data of Iron(III)–L-Amino Acid Perchlorates.

Complex	Band I[a] (nm)	Band II[b] (nm)	Band III[c] (nm)	Band IV[d] (nm)
L-alanine	200–425	444	628	952
L-proline	200–245	–	640	975
L-valine	200–425	480	620	962
L-leucine	200–425	480, 460	620	962
L-isoleucine	200–425*	–	620*	920*

[a]Methanolic solution spectra. [b]Solid state spectra, ref. 1, 4, and 13. [c]Solid state spectra, ref. 1 and 13. [d]Solid state spectra, ref. 1 and 13. *Methanolic solution spectra, R. N. Puri and R. O. Asplund, unpublished results.
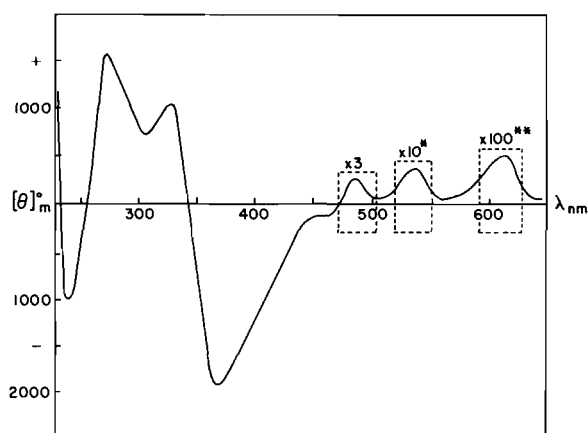

Fig. 2. The circular dichroic spectrum of the valine complex [Fe_3O(L-valine)$_6$(H_2O)$_3$]·(ClO$_4$)$_7$ in absolute methanol (c = 5×10^{-3} M, *c = 7.1×10^{-2} M, and **c = 2.8×10^{-1} M).

us. The CD spectra of the [Fe_3O(L-valine)$_6$(H_2O)$_3$]-(ClO$_4$)$_7$·3H_2O is shown in Fig. 2. It shows the extrema which are common to the complexes of L-isomers of alanine, proline, leucine, and isoleucine. The values of molar ellipticities [θ_m] corresponding to the various extrema are presented in Table I.

The electronic spectra of high spin iron(III) complexes (3d^5 system) containing the [Fe(III)O$_6$] unit have been discussed in considerable detail by Hush and Hobbs [14] and Gray [15]. In the ultraviolet region the electronic spectra of trinuclear iron(III) complexes in this work consist of a broad and high intensity band in the region 200–475 nm. This band probably represents an envelope of bands consisting of three bands at ca. 218 nm, ca. 250 nm, and ca. 311 nm. The band at ca. 218 nm is due to the presence of α-amino acid ligands in the complexes and corresponds to n → π* transition [16]. The absorption band at ca. 250 nm is simply a charge-transfer band. In the electronic spectra of [NH$_4$Fe(SO$_4$)$_2$·12H_2O], where Fe(III) is in octrahedral environment of water molecules, the observed absorption band at 317 nm [17] compares favorably

with the calculated value of 309 nm [18] and has been assigned to $^6A_1 \rightarrow {}^2T_1(^2G,\ ^2F,\ ^2F)$ transition [19]. The CD spectra of the complexes in this work exhibit an extremum at 311 nm. The origin of this extremum may be associated with a $^6A_1 \rightarrow {}^2T_1$ transition at ca. 311 nm in the electronic spectra of the complexes but is obscured by the high intensity band in the region 200–425 nm. The CD spectra of the polynuclear iron(III) complexes being discussed also contain extrema at 218, 245, and 267 nm (Table I). It is necessary to point out that although the extrema in the region 200–425 nm are capable of being resolved by the instrument used to scan the CD spectra, the instrument available to us and the methods employed to scan the electronic spectra of the complexes [1, 13] do not resolve the envelope of bands in the same wavelength region. If D-amino acids are used, the resultant CD spectra are the antipodes of those of the L-amino acids complexes within the experimental error. The spectra appear, on inspection, to be divided into two classes: (a) L-alanine, L-isoleucine, and L-proline for which the middle extrema (at 267 and 311 nm) are quite flat, ($\Delta\theta_m \approx$ 0–800), in fact for alanine they are not detected and we assume their presence only by analogy, and (b) L-valine and L-leucine for which these extrema have relatively much larger rotational strength ($\Delta\theta_m \approx$ 1,000–5,000). There are reports in the literature [20, 21] describing the relationship between rotational strength of the extremum arising due to n → π* transition and alkyl substituents on α-carbon atom of the L-amino acids in complexes containing transition metal ions other than iron, but the results are not uniform. The CD spectra of trinuclear iron(III)–L-amino acid complexes exhibit extrema at 345 and 378 nm (Table I). The electronic spectra of the known 3d^5 iron compounds [18, 19], containing the [Fe(III)O$_6$]$_{oct}$ unit, have been found to contain absorption bands at ca. 348 and 378 nm attributed to $^6A_1 \rightarrow {}^4T_2(^4D)$ and $^6A_1 \rightarrow {}^4E(^4D)$ transitions. Similar transitions in the electronic spectra of the complexes in this work are obliterated by the presence of the broad and high intensity band present in the region 200–425 nm. However, the rotational

strength of the extrema at 345 and 378 nm is far too high for the extrema to be associated with any kind of d–d transitions in the metal ions of the poly-nuclear complexes in this work. The rotational strength of the extrema at 345 and 378 nm is charac-teristic of charge-transfer transition between the cation and the anion [28]. It is therefore reasonable to conclude that the extrema at 345 and 378 nm are probably associated with composite of the sextet to quartet transitions, described above, in the d-electron manifold of the complexes and the charge-transfer transition between the cationic complexes and the perchlorate counter-ions. The CD spectra of trinuclear iron(III) complexes exhibit extrema at 459 and 475 nm, and the electronic spectra of the com-plexes derived from L-alanine, L-valine, and L-leucine show the presence of a band in the range 440–480 nm. The electronic spectra of the known compounds, e.g., $NaMgFe(C_2O_4)_3 \cdot 9H_2O$ [22], $(NH_4)_3Fe(C_3H_2O_4)_3$ [23], and $Fe(acac)_3$ [24] exhibit bands at 444, 441, and 454 nm respectively. These bands have been assigned to $^6A_1 \rightarrow {}^4A_1$, (^4A), ^4E transitions [14]. The correspondence between the extrema in the CD spectra and the maxima in the electronic spectra of $3d^5$ complexes in this work is noticeable. The most important absorption band in the spectra of iron(III)–L-amino acid complexes is exhibited at ca. 620 nm. Puri et al. [25–27] have shown that, in the case of Fe(III) complexes, the presence of this band not only signifies the presence of Fe(III) as $[Fe(III)O_6]_{oct}$ unit in the complexes but it also characterizes the presence of $[Fe_3O]^{7+}$ nucleus in such complexes. Furthermore, this absorption band is very useful in distinguishing among complexes containing the trinuclear oxobridged iron(III) unit, $[Fe_3O]^{7+}$, dinuclear dialkoxobridged iron(III) unit, $[Fe_2(OR)_2]^{4+}$, and unbridged $[Fe(H_2O)_6]^{3+}$ unit. All the complexes examined in this work show the presence of this characteristic band (Table II) at ca. 620 nm. The d–d transitions in octahedral complexes are both spin and multiplicity forbidden. However, in complexes, e.g., complexes in this work, the d–d transitions can take place by two mechanisms: (a) if the geometry around an iron atom does not conform to O_h symmetry, this results in the mixing of d and p orbitals of the complex, a transition then occurs between d levels with different amount of p-character, (b) in the course of normal vibrations of an octahedral complex, some of the molecules are distorted from O_h symmetry at any given time. This leads to vibronic coupling, i.e., electronic and vibrational wave functions mix in such a way that the product $\psi_{elec} \psi_{vib}$ has symmetry necessary for the integrand of the transition moment integral to be A_1; the d–d transitions can thus take place. The intensi-ties of bands resulting from such mechanisms are low. For a long time, efforts by the authors to locate the extremum at 620 nm in the CD spectra of the com-

plexes in this work were unsuccessful because of its very low intensity in their electronic spectra. How-ever, under more appropriate experimental conditions (Fig. 2), the CD spectra of all the trinuclear iron(III) complexes were found to exhibit an extremum at ca. 620 nm; the rotational strength of this extremum is, of course, very low. Another very important elec-tronic spectral characteristic of the complexes in this work is the presence of another low intensity band at ca. 909 nm. This band has been well characterized by Gray [15] and by the authors [2, 3, 25–27], and corresponds to the transition $^6A_1 \rightarrow {}^4T_1(^4G)$. This band, although, characteristic of $3d^5$ complexes containing $[Fe(III)O_6]_{oct}$ unit, is not capable of distinguishing polynuclear iron(III) complexes con-taining different types of oxo-bridges. Due to the limitations on the range of wavelength scan by the instrument available in our laboratory, we were unable to locate the corresponding extremum in the CD spectra of the complexes in this work.

Maximum optical activity is seen when the counter-anion is ClO_4^-. Other oxygen-containing anions show markedly reduced optical activities. Nitrate elicits about three percent of the activities of ClO_4^-, SO_4^{2-} less than one percent. The anions F^-, Cl^-, Br^-, and PF_6^- and BF_4^- gave complexes which were inactive. Complexes formed with anions other than ClO_4^- appear to exist in solution since they show the most characteristic 625 nm absorption band with unreduced intensity. At least in the case of complexes containing the SO_4^{2-} or NO_3^- as counterion, the reduced rotational strengths of the optima may be due to the reason that the heteroatoms in these oxy-anions have no non-bonding electrons in the valence shell of central hetero-atom, and charge-transfer transition, which must now take place by virtue of the interaction of d-electron manifold of the metal atom and the lone pair electrons of the oxyanions [28], is not quite adequate or there is a poor extension of the radial wave function of the lone pair orbitals for overlap with molecular orbitals of d-electron manifold of the irons. This in turn would affect the rotational strength of the optima due to the interaction of d-electron manifold with the ligands. Whatever the reasons, more quantitative data are needed to explain the effect of counter-ions on the rotational strength of various extrema in the CD spectra of these complexes.

The chirooptical properties of transition metal complexes are far less satisfactorily understood than those of simple organic molecules. This is due to the complicated nature of excitation processes in which the electronic transitions of the metal ions and metal–ligand charge transfer excitations superimpose on the electronic transitions of the organic ligand. Such interactions assume a diabolical character con-sidering the nature of polynuclear complexes under consideration. Metal complexes in general exhibit

four types of transitions: (a) the electronic transitions in the d-electron manifold (d—d transitions), (b) between the metal and the ligand (charge-transfer), (c) those which are essentially localized on the ligands, and (d) charge-transfer interaction between cation and the anions [10, 11, 16, 28—30]. The present work indicates that CD spectra of trinuclear oxo-bridged iron(III) perchlorates contain extrema that correspond to the electronic transitions described above. It has been pointed out by Mason *et al.* [31] that in the case of $[Co(en)_3]^{3+}$ the d-orbital wave functions extend to the carbon and hydrogen as well as the nitrogen atoms of the chelate ring. This has the effect of stabilizing the t_{2g} electrons by partial delocalization into antibonding σ-orbitals covering all atoms of ethylene-diamine rings. Their conclusions are based on the experimental value of Dq and B for $[Co(NH_3)_6]^{3+}$ and comparison with those of the $[Co(en)_3]^{3+}$. We are tempted to extend this analogy to the present complexes, *i.e.*, the $d\pi$-electron manifold of the irons interacts with $p\pi$-electron manifold of the carboxylate ion of the zwitterionic L-amino acids and this in turn may further be stabilized by partial delocalization into antibonding σ-orbitals of the α-carbon and hydrogen atoms of L-amino acid ligands. Such interactions appear very attractive because the geometry of the $[Fe_3O]^{7+}$ nucleus with C_3 axis, present in the complexes in this work, permit substantial overlap of $d\pi$-electron cloud of irons with $p\pi$-electron clouds of the bridging oxygens, although not to the extent as in the case of linear Fe—O—Fe systems with C_2 axis. The enormous amount of magnetic data gathered by the authors [1—4, 25—27] and the fact that trinuclear iron(III)—L-amino acid complexes are antiferromagnetic in character support the conclusions outlined above. In summary, from the data presented in Tables I and II and the foregoing discussion, it is reasonable to conclude that chirooptical properties of trinuclear oxobridged iron(III)—L-amino acid perchlorates are largely due to the perturbation in the overall charge-transfer manifold of the complexes resulting from interactions with asymmetric carbon atom of α-amino acids. There are two reasons for this conclusion: the extrema in the CD spectra are approximately equivalent to the expected electronic transitions and they are dependent on the presence of an asymmetric carbon atom. Complexes with symmetric amino acids, such as glycine, and of racemic mixtures exhibit, as expected, no detectable activity. Efforts are underway to analyze and understand the reasons

for the sign of the extrema in the CD spectra of the complexes in this work and the results will be presented in a future communication.

References

1 W. F. Tucker, R. O. Asplund and S. L. Holt, *Arch. Biochem. Biophys.*, *166*, 433 (1975).
2 R. Puri, R. O. Asplund and S. L. Holt, *J. Coord. Chem.*, in press.
3 R. Puri and R. O. Asplund, *Inorg. Chim. Acta*, in press.
4 E. M. Holt, S. L. Holt, R. O. Asplund, W. F. Tucker and K. J. Watson, *J. Am. Chem. Soc.*, *96*, 2621 (1974).
5 R. V. Thundathil, E. M. Holt, S. L. Holt and K. J. Watson, *J. Am. Chem. Soc.*, *99*, 1818 (1977).
6 R. B. Martin in 'Metal Ions in Biological Systems', Vol. I, ed. H. Sigel, Marcel Dekker, New York, 1974.
7 K. Kawaski, J. Yoshii and M. Shibata, *Bull. Chem. Soc. Japan*, *43*, 3819 (1970).
8 J. M. Tsangaris and R. B. Martin, *J. Am. Chem. Soc.*, *92*, 4255 (1970).
9 L. I. Katzin and E. Gulyas, *J. Am. Chem. Soc.*, *91*, 6940 (1960).
10 S. F. Mason, *Inorg. Chim. Acta Rev.*, *2*, 89 (1968).
11 B. Bosnich, *Acc. Chem. Res.*, *2*, 266 (1969).
12 E. C. DeVore, S. L. Holt, R. O. Asplund and A. W. Catalano, *Arch. Biochem. Biophys.*, *146*, 658 (1971).
13 W. F. Tucker, *Ph. D. Dissertation*, The University of Wyoming, U.S.A., 1973.
14 N. S. Hush and R. J. M. Hobbs in 'Progress in Inorganic Chemistry', Vol. 10, Ed. F. A. Cotton, Wiley, New York and London, 1968, pp. 326—347.
15 H. B. Gray, *Advan. Chem. Ser.*, *No. 100*, 365 (1971).
16 P. Crabbe, 'ORD and CD in Chemistry and Biochemistry', pp. 54—58 and 145—154, Academic Press, New York, 1972.
17 R. Pappalardo, *Nuovo Cimento*, *8*, 955 (1958).
18 W. Moffit and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, *7*, 197 (1956).
19 W. Low and G. Rosengarten, *J. Mol. Spectry.*, *12*, 319 (1964).
20 J. M. Tsangaris, J. WenChang and R. B. Martin, *J. Am. Chem.*, *91*, 276 (1969).
21 L. I. Katzin and E. Gulyas, *J. Am. Chem. Soc.*, *90*, 247 (1968).
22 T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, *35*, 1809 (1961).
23 W. E. Hatfield, *Inorg. Chem.*, *3*, 841 (1963).
24 T. S. Piper and R. L. Carlin, *Inorg. Chem.*, *2*, 260 (1963).
25 R. Puri and R. O. Asplund, *J. Coord. Chem.*, in press.
26 R. Puri and R. O. Asplund, *Inorg. Chim. Acta*, in press.
27 R. Puri and R. O. Asplund, *Experientia*, in press.
28 E. Larson and S. F. Mason, *J. Chem. Soc. (A)*, 313 (1966).
29 B. Bosnich, 'Advanced Study Institute on Fundamental Aspects and Recent Developments in ORD and CD', Pisa (Italy), September 1971, *Abstracts of Papers*, p. 37.
30 S. F. Mason, *ibid., Abstracts of Papers*, pp. 19, 39.
31 S. F. Mason and B. J. Norman, *Chem. Comm.*, 41 (1965).