

Figure 1. The molecular ellipticity  $[\theta]$  (left-hand scale) and ordinary absorption  $\epsilon$  (right-hand scale) of (—)(*S*)-4-deuterio[2.2]paracyclophane in methanol. The base line for ellipticity shown by the broken lines was obtained by replacing the sample with the same concentration of [2.2]paracyclophane.

A large number of published CD spectra for 4-substituted [2.2]paracyclophanes<sup>5,6</sup> show that the sign and magnitude of long wavelength rotatory strength for a given chirality vary with the transition electric dipole direction in the trisubstituted benzene ring.<sup>7</sup> Platt's spectroscopic moments<sup>8</sup> adequately predict this direction. Therefore, the perturbation that gives rise to rotatory strength in these 4-substituted [2.2]paracyclophanes must have an electronic origin. That such electronic effects would be absent for **1** can be concluded from the observation that the long wavelength uv vapor spectrum of deuteriobenzene, like benzene, lacks a 0-0 band.<sup>9</sup> Alternatively a vibronic coupling model can be defined<sup>10</sup> which again accounts for a turning of the benzene transition dipole direction.

The experimental circular dichroism for compound **1**<sup>11</sup> shown in Figure 1 has a number of notable features. The magnitude of molecular ellipticity<sup>12,13</sup> in the <sup>1</sup>L<sub>b</sub> bands (280–330 nm) is about 1/100 of that for (+)-(*S*)-4-methyl[2.2]paracyclophane.<sup>5</sup> The vibronically induced CD in more massively substituted [2.2]paracyclophanes is probably larger. But unless the vibronic CD contribution varies as an inordinately high power of the

(4) Mass spectra were kindly furnished by Professor W. Weber at the University of Southern California.

(5) M. J. Nugent and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, **91**, 4556 (1969).

(6) H. Falk, P. Reich-Rohrwig, and K. Schloegl, *Tetrahedron*, **26**, 511 (1969).

(7) O. E. Weigang, Jr., and M. J. Nugent, *J. Amer. Chem. Soc.*, **91**, 4555 (1969).

(8) (a) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951); (b) J. Petruska, *ibid.*, **34**, 1120 (1961).

(9) F. M. Garforth and C. K. Ingold, *J. Chem. Soc.*, 483 (1948).

(10) M. A. Hassloch, M. J. Nugent, and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, **96**, 2619 (1974).

(11) Compound **1** was purified by recrystallization and tlc on silver nitrate-coated silica gel until the CD was constant. Measurements were carried out on a Cary 60 spectropolarimeter with a 6001 CD accessory. The uv spectrum of **1** is identical with that of [2.2]paracyclophane.

(12) The observed order of magnitude is the same as found for 1-deuterio- $\alpha$ -fenchocamphoronequinone.<sup>13</sup>

(13) W. C. M. C. Kokke, Doctoral Thesis, University of Leiden, 1973.

mass, this contribution would be much too small to account for the CD of the <sup>1</sup>L<sub>b</sub> bands observed previously.<sup>5,7</sup> This result is consistent with the evidence that an electronic perturbation, operative even in a vibrationless molecule, is responsible for the optical activity in these cases. The shorter wavelength component of the <sup>1</sup>L<sub>b</sub> band pair appears as a positive contribution to the edge of the highly negative <sup>1</sup>L<sub>a</sub> region. As in some other instances<sup>5,6</sup> the sign of the <sup>1</sup>L<sub>a</sub> band dominates.

The <sup>1</sup>L<sub>a</sub> region (240–280 nm) in Figure 1 shows a signed CD that is reversed from the unchanging sign for the same transition in other *S*-4-substituted [2.2]paracyclophanes.<sup>5,6,14</sup> If the CD of these shorter wavelength bands is indeed dominated by vibronic rather than purely electronic perturbations,<sup>7</sup> it may be relevant that Figure 1 shows the one CD where the mass at the 4 position is much less than the ethylene bridges.

**Acknowledgment.** This work was supported in part by NSF Grant GP-16356; [2.2]paracyclophane was generously supplied by Union Carbide Corp.

(14) This observation shows that trace amounts of optically active *S*-substituted [2.2]paracyclophane contaminants are not responsible for the CD of **1**.

(15) NSF-URP Fellow 1971.

Phillip H. Hoffman,<sup>15</sup> Edith C. Ong  
Oscar E. Weigang, Jr., Maurice J. Nugent\*  
Department of Chemistry, Tulane University  
New Orleans, Louisiana 70118  
Received November 16, 1973

### Preparation and Properties of Iron(III)-Amino Acid Complexes. Iron(III)-Alanine, a Possible Ferritin Analog

Sir:

Spiro, Saltman, and coworkers have shown that it is possible to produce an iron-containing polymer of a molecular weight of approximately 150,000 from bicarbonate-hydrolyzed ferric nitrate solutions.<sup>1-4</sup> A similar result is found for hydrolyzed iron-citrate solutions.<sup>5,6</sup> The physical properties of the polymer, Tables I and II, suggest that its constitution is essentially that of the ferritin core. Based primarily upon low angle X-ray scattering work, Brady, *et al.*,<sup>3</sup> have suggested that the structure of the iron-containing polymer and thus the ferritin core consists of polymerically bound tetrahedral [FeO<sub>2</sub>(OH)<sub>2</sub>] units. Gray<sup>7</sup> has taken issue with this model pointing out that in the electronic spec-

(1) T. G. Spiro, S. E. Allerton, J. Renner, A. Terzis, R. Bils, and P. Saltman, *J. Amer. Chem. Soc.*, **88**, 2721 (1966).

(2) S. E. Allerton, J. Renner, S. Colt, and P. Saltman, *J. Amer. Chem. Soc.*, **88**, 3147 (1966).

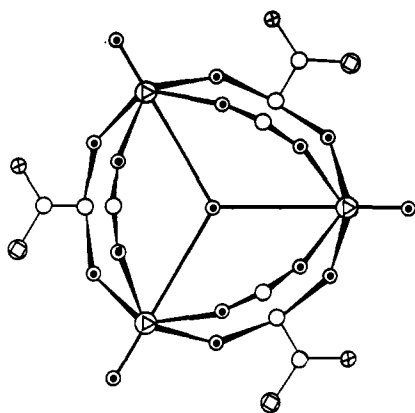
(3) G. W. Brady, C. R. Kurkjian, E. F. X. Lyden, M. B. Robin, P. Saltman, T. Spiro, and A. Terzis, *Biochemistry*, **7**, 2185 (1968).

(4) B. A. Sommer, D. W. Margerum, J. Renner, P. Saltman, and T. G. Spiro, *Bioinorg. Chem.*, **2**, 295 (1973).

(5) T. G. Spiro, L. Pape, and P. Saltman, *J. Amer. Chem. Soc.*, **89**, 5555 (1967).

(6) T. G. Spiro, G. Bates, and P. Saltman, *J. Amer. Chem. Soc.*, **89**, 5559 (1967).

(7) H. B. Gray, *Advan. Chem. Ser.*, No. 100, 365 (1971).



**Figure 1.** Schematic representation of the molecular structure of  $[\text{Fe}(\text{alanine})_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7$ . The  $\text{ClO}_4^-$  have been omitted from the figure. In addition the  $\alpha$ -carbon and residues have been omitted from the forward-projecting carboxylates for clarity. Legend:  $\oplus$ , iron;  $\circ$ , oxygen;  $\odot$ , methyl;  $\otimes$ , quaternary nitrogen;  $\circ$ , carbon.

**Table I.** Spectral Parameters for Iron(III) Polymers

Compound	$\nu_{\text{max}}$ , $\text{cm}^{-1}$ ( $\epsilon$ , $\text{cm}^{-1}/\text{Fe}$ )
$[\text{Fe}(\text{alanine})_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7^a$	10,250 (3), 16,000, 19,500, 22,500
$[\text{FeOFe}]^{4+ b}$	11,200 (3), 18,400 (40), 21,000 (25), 22,000 (2), 22,000 (2), 24,700 (100)
$[\text{Fe} \begin{array}{c} \text{R} \\ \diagdown \text{O} \diagup \\ \text{O} \\ \diagup \text{O} \diagdown \\ \text{R} \end{array} \text{Fe}]^{4+ c}$	10,700 (1), 14,100 (2), 23,900 (2350), 28,300 (3150)
Spiro-Saltman Ball <sup>d</sup>	11,000 (0.21), 15,600 (0.32), 20,000 (4.4)
Ferritin <sup>e</sup>	10,900

<sup>a</sup> At 80°K. <sup>b</sup> As  $\text{enH}_2[(\text{FeHEDTA})_2\text{O}] \cdot 6\text{H}_2\text{O}$  at 296°K: H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Amer. Chem. Soc.*, **94**, 2683 (1972). <sup>c</sup> As  $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)_2]$ , ref 8. <sup>d</sup> Reference 3. <sup>e</sup> Reference 7.

**Table II.** Magnetic and Mössbauer Data for Iron(III) Polymers

Compound	$\mu/\text{Fe}^{3+}(300^\circ\text{K})$	$-J$ , $\text{cm}^{-1}$	$\delta^a$	$E\Delta_q$
$[\text{Fe}(\text{alanine})_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7^b$	3.20	31 <sup>c</sup>	0.68	0.51
$[\text{Fe}_3\text{O}]^{7+ d}$	$\sim 3.40$	$\sim 30$	0.42–0.53	0.45–0.72
$[\text{FeOFe}]^{4+ e}$	$\sim 2.0$	$\sim 90$	0.63–0.79	0.92–1.82
$[\text{Fe} \begin{array}{c} \text{H} \\ \diagdown \text{O} \diagup \\ \text{O} \\ \diagup \text{O} \diagdown \\ \text{H} \end{array} \text{Fe}]^{4+ f}$	5.2	8		1.00
Spiro-Saltman Ball <sup>g</sup>	3.1	31	0.66	0.67
Ferritin <sup>g</sup>	3.81	30	0.65–0.68	0.60–0.74

<sup>a</sup>Reported in mm/sec relative to sodium nitroprusside. <sup>b</sup>This work. <sup>c</sup>Based on a trimer and  $g = 2$ : G. J. Long, W. T. Robinson, W. P. Tappmeyer, and D. L. Bridges, *J. Chem. Soc., Dalton Trans.*, 573 (1973). <sup>d</sup>As basic iron acetate, reference in footnote c,  $\delta$  relative to iron foil. <sup>e</sup>H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Amer. Chem. Soc.*, **94**, 2683 (1972). <sup>f</sup>H. J. Schugar, G. R. Rossman, and H. B. Gray, *ibid.*, **91**, 4564 (1969). <sup>g</sup>Reference 3.

trum of the "Spiro-Saltman Ball" there are no absorption maxima, in the visible region, which are attributable to tetrahedrally coordinated Fe(III) but only those which may be ascribed to octahedrally coordinated Fe(III). For the case of ferritin, things are not so clear cut as charge transfer obliterates all but the very lowest energy absorption maximum.<sup>7</sup> In this communication we wish to present evidence which supports Gray's contention that octahedral coordination is present in both the "Spiro-Saltman Ball" and ferritin and suggests that the basic unit in these species may be a trimer.

$[\text{Fe}(\text{C}_3\text{NO}_2\text{H}_7)_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7$  is prepared by dissolving perchloric acid washed  $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  and *d*- or *l*-alanine in water in a 1:2 ratio. Slow evaporation produces a red-brown crystalline product which analyzes correctly for the above formula.

$[\text{Fe}(\text{C}_3\text{NO}_2\text{H}_7)_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7$  crystallizes in the monoclinic space group  $P2_1$ , with four molecules in a unit cell (two molecules per asymmetric unit) having dimensions:  $a = 20.114$  (1),  $b = 15.840$  (8),  $c = 17.409$  (9) Å;  $\beta = 104^\circ 16$  (5);  $V = 5384.9$  Å<sup>3</sup>;  $D_{\text{obsd}} = 1.806$ ,  $D_{\text{calcd}} = 1.82$  cm<sup>-3</sup>.

Three dimensional X-ray data were obtained by use of a Picker automated four-circle diffractometer and  $\text{Mo K}\alpha$  radiation. A total of 9132 independent reflections were measured, of which 4509 were judged to be observed. The structure was solved by heavy atom methods. Full-matrix least-squares refinement has now reached  $R = 0.15$ .

The complex is trinuclear (iron acetate structure) with the central oxygen atom lying on the plane of the three irons and 1.92 Å from each of them (Figure 1). Each pair of iron atoms is 3.32 Å apart and bridged by two alanines through the oxygens of the carboxyl groups. The sixth coordination site of the octahedral iron atoms is filled by the oxygen of a water molecule at a distance of 2.07 Å. The nitrogen atoms of each alanine have a number of neighboring  $\text{ClO}_4^-$  oxygen atoms close enough for hydrogen bonding. Our investigations indicate that the structure of the iron-containing core is a common one for complexes of Fe(III) with amino acids and also appears to be present when the complexing agent is a more complex species (e.g., glycylglycylglycine).

Table I contains the spectral parameters for  $[\text{Fe}(\text{alanine})_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7$ , for other known bridged structures, and for the "Spiro-Saltman Ball" and ferritin. While the first three members of this table all exhibit different types of bridging, all are basically octa-

hedral in structure, when the entire molecule in which they occur is considered. This accounts for the similarity in their spectra. All five species in Table I have in common an absorption maximum at 10,000–11,000  $\text{cm}^{-1}$ . In addition the "Spiro-Saltman Ball" exhibits higher energy maxima as do the first three species. This comparison tends to support Gray's<sup>8</sup> contention that the Fe(III) in the "Spiro-Saltman Ball" is exclusively octahedrally coordinated and that some octa-

(8) C. H. S. Wu, G. R. Rossman, H. B. Gray, G. S. Hammond, and H. J. Schugar, *Inorg. Chem.*, **11**, 990 (1972).

hedrally coordinated Fe(III) exists in ferritin. While perhaps fortuitous it can also be pointed out that of the three possible oxo, hydroxo-bridged models the absorption spectrum of the Fe-alanine compound most closely resembles that of the "Spiro-Saltman Ball."

In Table II we have tabulated the magnetic results and Mössbauer parameters for the three model systems, the "Spiro-Saltman Ball" and ferritin. Without question both the  $\mu/\text{Fe}^{3+}$  and the  $-J$  for the Fe(III)-alanine complex most closely resemble the values found for the latter two members of Table II. In addition the similarity of these species is reinforced by the Mössbauer data. This suggests that the  $[\text{Fe}_3\text{O}]^{7+}$  unit must be considered as a strong candidate for the basic "monomeric" unit in both the "Spiro-Saltman Ball" and ferritin.

**Acknowledgment.** This research was supported by the National Institutes of Health, the North Atlantic Treaty Organization, and the Statens Naturvidenskabelige Forskningsrod.

Elizabeth M. Holt, Smith L. Holt\*  
William F. Tucker, R. Owen Asplund

Department of Chemistry, University of Wyoming  
Laramie, Wyoming 82071

Kenneth J. Watson

Kemisk Laboratorium IV, H. C. Ørsted Institute  
Copenhagen, Denmark

Received October 12, 1973

## Use of the CNDO Method in Spectroscopy. XI. Photoelectron Spectra

Sir:

The most widely applied theoretical method in the assignment of bands in photoelectron (PE) spectra and in their interpretation<sup>1</sup> is based on the use of Koopmans' theorem.<sup>2</sup> Although many authors have long been aware of the shortcomings of this procedure,<sup>3</sup> the lack of reasonably reliable and readily applied methods for the calculation of the doublet states of the molecular ions has retarded progress in the interpretation of PE spectra and forced many authors into the use of Koopmans' theorem in spite of its undesirability.

We have now developed two semiempirical methods for calculation of the energies (and wave functions) of doublet states, which are readily applicable to the calculation of the molecular ions of molecules of first-row elements with closed shell ground states. Both methods are based on the CNDO/S method;<sup>4</sup> the first<sup>5</sup> is quite analogous to the closed shell CNDO/S method, using a SCF calculation of the ionic ground state by the Roothaan open shell restricted Hartree-Fock formalism,<sup>6</sup> followed by a limited CI calculation using singly excited configurations. The second method<sup>7</sup> involves the direct

SCF calculation of excited doublet states, again by the Roothaan method.<sup>6</sup> In this communication we report the first application of these methods to PE spectra.

The PE spectral information is usually reported as the ionization potential from the molecular ground state to the ion state  $J$ ; this quantity can be decomposed into two terms

$$I_J = I_0 + X_J \quad (1)$$

where  $I_0$  is the ionization potential to the ion ground state and  $X_J$  the energy of the ion state  $J$  above its ground state. Ionization potentials are most commonly obtained by using Koopmans' theorem; the CNDO/S method appears to be the best of the common semiempirical methods (without special parametrization) for obtaining ionization potentials,<sup>8</sup> but the values obtained are usually significantly too high. The SCF procedure for the ion ground state gives another independent estimate of the vertical ionization potential as the difference of the total energy of the ground states of the neutral molecule and the ion. The ionization potentials so obtained are generally somewhat below the Koopmans' theorem values but are still uniformly high. These results are summarized in Table I.

Table I. Calculated First Ionization Potentials by SCF Procedure and Koopmans' Theorem

Molecule	Ionization potential		
	SCF	Koopmans' theorem	Exptl
Benzene	10.4	10.8	9.24 <sup>a</sup>
s-Trifluorotriazine	11.3	11.5	10.3 <sup>b</sup>
s-Triazine	12.1	12.5	10.41 <sup>b</sup>
s-Trifluorotriazine	13.2	13.5	12.0 <sup>b</sup>
Pyridine	10.5	10.8	9.31 <sup>a</sup>
Pyrimidine	11.1	11.4	9.32 <sup>c</sup>
Pyrazine	10.6	10.9	9.22 <sup>c</sup>
Pyridazine	11.0	11.0	8.71 <sup>c</sup>

<sup>a</sup> Reference 12. <sup>b</sup> Reference 15. <sup>c</sup> Reference 14.

In what follows we shall ignore the first term of eq 1 and restrict ourselves to a consideration of the second term,  $X_J$ , i.e., the relative positions of the bands in the PE spectrum or the spacing of the doublet states of the ion. The expression for the PE cross section is given as<sup>9</sup>

$$\sigma_{J0} = \frac{8\pi^3 e^3 \nu}{3c} |\langle {}^1\Psi_0 | \sum_i \mathbf{r}_i | {}^1\Psi_J \rangle|^2$$

where  $e$ ,  $\nu$ , and  $c$  are the electronic charge, the frequency of the ionizing radiation, and the velocity of light, respectively.

In the present work we take  ${}^1\Psi_0$  as a single Slater determinant of order  $n$ .  ${}^1\Psi_J$  is a proper singlet eigenfunction of an excited state of the  $n$  electron system in which  $n - 1$  electrons occupy molecular orbitals in the usual sense of the word and the remaining one-electron wave function is a proper wave function for a free electron.<sup>10</sup> If the molecular orbitals making up  ${}^1\Psi_0$  and  ${}^1\Psi_J$  are orthogonal, one is led to the conclusion that

(8) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **50**, 563 (1969).

(9) L. L. Lohr and M. B. Robin, *J. Amer. Chem. Soc.*, **92**, 7241 (1970).

(10) (a) D. R. Bates, U. Öpic, and G. Poats, *Proc. Phys. Soc., London, Sect. A*, **66**, 1113 (1953); (b) A. Dalgarno, *ibid.*, **65**, 663 (1952).

(1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., Chapter 1 and Chapter 4.

(2) T. A. Koopmans, *Physica*, **1**, 104 (1933).

(3) Cf. ref 1, pp. 6-7; cf. also M. H. Palmer, A. J. Gaskell, and R. H. Findlay, *Tetrahedron Lett.*, **47**, 4659 (1973).

(4) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968); R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, **26**, 131 (1972).

(5) H. M. Chang and H. H. Jaffé, *Chem. Phys. Lett.*, **23**, 146 (1973).

(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

(7) H. H. Jaffé, H. M. Chang, and C. A. Masmanidis, *J. Comput. Phys.*, in press.