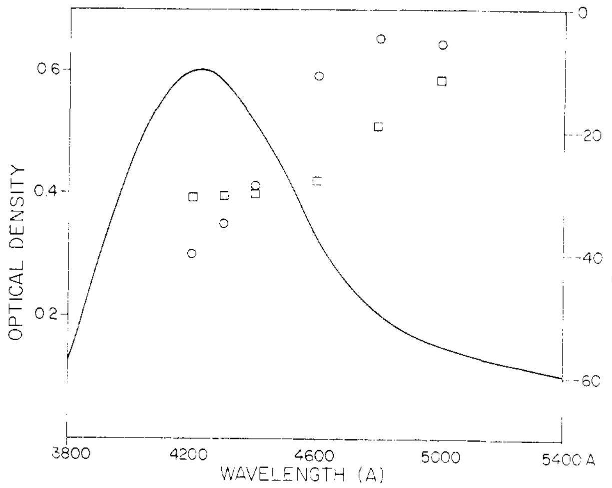


Figure 2. Absorption spectrum and the effects of external field. Circles correspond to the component parallel to the external field and squares to the perpendicular component. ΔI is the change in transmitted light induced by the external field. I is the optical transmission of the solution without the external field. The data between 4400 to 5000 Å are not discussed in the text. Concentrations: pyridine, $1.8 \times 10^{-2}\,M$; iodine, $1 \times 10^{-4}\,M$; solvent, cyclohexane; field strength, 6.8×10^4 V/cm at peak value.

(lesser transmission) than the absorption perpendicular to the field. This result is consistent with structure I.[10] Quantitative treatment of the data on several solutions of the pyridine–iodine complex show that the 4200-Å band is polarized very nearly parallel to the dipole moment of the complex and that the changes in transition probability induced by the electric field are not negligible. Data between 4400 and 5000 Å can also be explained satisfactorily by a consideration of changes in the dipole moment upon excitation.[8,9]

These results conclusively show that studies of effects of electric fields on the absorption of donor–acceptor complexes can yield valuable information on the geometry in solution and the dipole moment in the excited state. Details of this work and work on other donor–acceptor complexes will be communicated in the near future.

Acknowledgment. I am indebted to Professors W. B. Miller, III and D. C. Hofer for helpful suggestions. I wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[10] A conformation in which the iodine molecule is located along an axis perpendciular to the plane of pyridine is also consistent with these data. Such a possibility can, however, be ruled out in the present case because pyridine is an n and not a π donor.

G. Krishna Vemulapalli
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

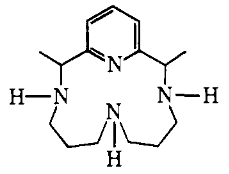
Received October 2, 1970

Five-Coordinate High-Spin Iron(II) Complexes of Synthetic Macrocyclic Ligands

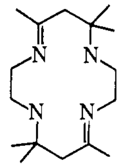
Sir:

A new synthetic class of complexes having five-coordinate high-spin iron(II) bound to macrocyclic ligands has been prepared. These species have structural features similar to those of certain compounds of biological significance, notably deoxyhemoglobin and deoxymyoglobin. We report here the synthesis and characterization of nine compounds of this new class, involving three ligands of varying degrees of unsaturation. In view of these results we feel that the five-coordinate high-spin configuration for Fe(II) should no longer be considered rare and that the binding of Fe(II) in the extremely important naturally occurring hemes properly fits into the systematic chemistry of that species. It has also been found that the Mössbauer parameters of the five-coordinate Fe(II) compounds fall into a unique range with unusually large quadrupole splitting.

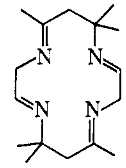
The ligands are (a) *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (CRH, structure I); (b) 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-diene (1,7 CT, structure II); and (c) 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),3,7,10-tetraene (1,3,7,10 CT, structure III). Complexes of CRH[1] and 1,7 CT[2] with other metal ions are well known. Each ligand presents a square array of nitrogen atoms with the metal ion nominally in the center. The new iron compounds with these ligands are given in Table I, together with some of their more pertinent physical properites. Details will appear later.



CRH
I



1,7 CT
II



1, 3, 7, 10 CT
III

Evidence supporting a five-coordinate square-pyramidal geometry of the [Fe(1,7 CT)X]ClO$_4$ and [Fe(1,3,7,10 CT)X]ClO$_4$ series (X = Cl, Br, I) involves their stoichiometries, magnetic moments, molar conductivities, infrared spectra, and d–d electronic spectra. The infrared spectra indicated the absence of water or other hydroxylic species and showed only free perchlorate ions. Conductivity data indicate uniunivalent electrolytes in nitromethane.[3] Most helpful, the d–d electronic spectra show that the strong tetragonal distortion (C_{4v} symmetry) present in these five-coordinate complexes produces a very large splitting of the ^{5}E spectroscopic term state (derived from O_h symmetry) into $^5B_1$ and $^5A_1$ states (corresponding to the $d_{x^2-y^2}$ and d_{z^2} orbitals of the one-electron orbital description). This is consistent with the behavior of other metal ions.[4] Careful spectroscopic measurements on these complexes (solid state and nitromethane solution; 3.0–25-kK region) reveal two broad weak d–d transitions near 5.0 and 12.5 kK for each compound (Table I). The higher energy absorption occurs at the same energy for each complex and is assigned to the transition to the B$_1$ ($d_{x^2-y^2}$) state. The position of the lower energy absorption (transition to A$_1$ (d_{z^2})) is dependent upon the field strength of the axial ligand.

---

(1) D. H. Busch, *Helv. Chim. Acta, Fasciculus extraordinarius Alfred Werner*, 174 (1967).
(2) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).
(3) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).
(4) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 6, 1092 (1967).

Table I. Physical Properties of Some New Five-Coordinate Iron(II) Complexes

				Mossbauer parameters	
	Λ_M	μ_{eff}, BM[c]	d–d electronic spectra[d]	δ, mm/sec[e]	ΔE_Q, mm/sec
$[Fe(1,7\ CT)Cl]ClO_4$	95[a]	5.05	4.7 (7); 12.2 (5)	1.15	3.78
$[Fe(1,7\ CT)Br]ClO_4$	106[a]	5.11	~5 (~5); 12.2 (4.9)	1.14	3.81
$[Fe(1,7\ CT)I]ClO_4$	93[a]	5.15	<5 (~4); 12.2 (4)	1.12	3.34
$[Fe(1,3,7,10\ CT)Cl]ClO_4$	97[a]	5.00	4.65 (3); 11.62 (3)	1.13	3.60
$[Fe(1,3,7,10\ CT)Br]ClO_4$	99[a]	5.14	4.76 (3); 11.66 (3)	1.14	3.78
$[Fe(1,3,7,10\ CT)I]ClO_4$	102[a]	5.10	~5; 11.65	1.10	3.79
$[Fe(CRH)Cl]Cl$	110[b]	5.20		1.11	3.72
$[Fe(CRH)Br]Br$	92[b]	5.11		1.12	3.84
$[Fe(CRH)I]I$	102[b]	5.05		1.08	3.84

[a] Molar conductance obtained in purified nitromethane under N_2 atmosphere; concentrations were in the range 1.5×10^{-3}–0.97×10^{-3} *M*. [b] Obtained in absolute methanol under N_2 atmosphere; concentrations $\sim 10^{-3}$ *M*. [c] Obtained at room temperature using the Faraday technique. [d] Obtained in nitromethane under N_2 atmosphere, absorption maxima in kilokaisers, molar extinction coefficients are given in parentheses. [e] Values are with respect to sodium nitroprusside standard.

The Mössbauer parameters of these five-coordinate complexes were obtained during the course of an extensive investigation of several series of iron complexes of varying coordination number, geometry, spin state, and oxidation state.[5] The strong axial perturbation in these five-coordinate complexes yields a unique range of Mössbauer parameters which appear to be characteristic of iron(II) in this environment. For the five-coordinate $[Fe(1,7\ CT)X]ClO_4$ and $[Fe(1,3,7,10\ CT)X]ClO_4$ series, the isomer shifts (δ) are in the characteristic range for high-spin Fe(II), in agreement with the magnetic data. Quadrupole splitting values (ΔE_Q) are consistently large (3.3–3,8 mm/sec), and together with the δ values form a set of parameters unique among iron coordination compounds. The range of ΔE_Q values for these compounds is the highest yet recorded for iron. The more familar high-spin Fe(II) complexes have quadrupole splittings in the range 2.0–3.0 mm/sec;[6] the ΔE_Q values of so-called ionic salts are normally between 2.5 and 3.5 mm/sec.[7] The relative contributions of the electric field gradient due to the dissymmetry of the electron population and to the ligand environment will be discussed in another paper.

Very few previously reported iron complexes have ΔE_Q values greater than 3.5 mm/sec. One of these is a pyrazolylborate which is a high-spin Fe(II) compound;[8] another is a five-coordinate low-spin iron(III) phthalocyanine complex.[9]

The characteristic range of Mössbauer parameters for five-coordinate high-spin Fe(II) can be helpful in identifying this configuration in other iron compounds. For example, in the series $Fe(CRH)X_2$ (X = Cl, Br, I) experimental difficulties limit the value of other physical data in attempts to assign the coordination number. For each of these compounds, δ is in the characteristic range for high-spin Fe(II) and ΔE_Q is in the range 3.3–3.8 mm/sec. In the absence of a complete X-ray structural determination, Mössbauer spectra appear to be the most convenient means of establishing the presence of five-coordinate high-spin Fe(II) in the solid state.[10]

Acknowledgment. The financial support of the National Institute of General Medical Sciences of the U. S. Public Health Service (Grant No. GM-10040) and of the National Science Foundation is gratefully acknowledged. Part of the information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U. S. Atomic Energy Commission.

---

(5) To be reported. Room-temperature Mössbauer spectra were taken with a conventional constant-acceleration time-mode spectrometer, calibrated with sodium nitroprusside, iron metal, and α-Fe_2O_3.

(6) L. May, "The Mössbauer Effect and Its Application in Chemistry," R. H. Herber, Ed., American Chemical Society Publications, Washington, D. C., 1967, p 54.

(7) J. Danon, "Chemical Applications of Mössbauer Spectroscopy," V. I. Goldanskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, pp 233–241.

(8) J. P. Jesson, J. F. Weiher, and S. Trofimenko, *J. Chem. Phys.*, **48**, 2058 (1968).

(9) R. Taube, H. Drevs, E. Fluck, and P. Kuhn, *Z. Anorg. Allg. Chem.*, **364**, 297 (1969).

(10) The experimental correlations provide the best justification for the kind of generalization we suggest here. ΔE_Q will depend on the nature of the ground state in C_{4v} symmetry; under a tetragonal distortion the $^5T_2$ state (O_h) is split into $^5B_2$ and ^5E states. The ordering of these states will depend upon the sign of the tetragonal splitting. Actually, the magnitudes of the contributions to the quadrupole splitting from a 3d electron in the $^5B_2$ or in the ^5E state are equal, but the electric field gradients associated with the two states have opposite signs. When the contribution to ΔE_Q from the ligand-field dissymmetry is included, somewhat different splittings may occur for the two states. In all the cases reported here, the monodentate ligand on the pseudofourfold axis is of much weaker ligand-field strength than is the in-plane macrocycle. Consequently the ^5E state is expected to lie lowest.

* Address correspondence to this author.

Philip H. Merrell, Virgil L. Goedken, Daryle H. Busch*
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

J. A. Stone
Savannah River Laboratory, E. I. du Pont de Nemours and Company
Aiken, South Carolina 29801

Received August 29, 1970

Geldanamycin. I. Structure Assignment

Sir:

The ansamycin antibiotics have aroused considerable interest, both on account of their unusual *ansa* structures and because some of these compounds show marked antiviral activity as well as potent inhibition of DNA-dependent RNA polymerase.[1] The members of this class of antibiotics reported until now (rifamycins,[2] streptovaricins,[3] tolypomycins[4]) have all contained naphthoquinone nuclei. In the present report we

---

(1) A review of ansamycins: K. L. Rinehart, Jr., submitted for publication.

(2) W. Oppolzer, V. Prelog, and P. Sensi, *Experientia*, 20, 336 (1964).

(3) K. L. Rinehart, Jr., H. H. Mathur, K. Sasaki, P. K. Martin, and C. E. Coverdale, *J. Amer. Chem. Soc.*, **90**, 6241 (1968).

(4) T. Kishi, S. Horada, M. Asai, M. Muroi, and K. Mizuno, *Tetrahedron Lett.*, 97 (1969).