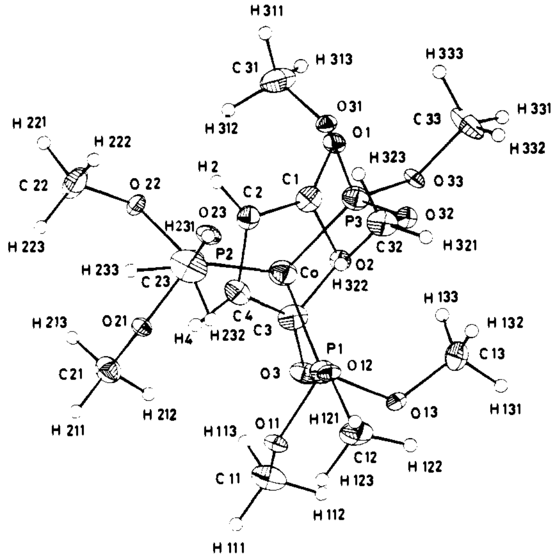

Figure 1. Molecular structure of tris(trimethyl phosphite)(maleic anhydride)cobalt(0).

molecular structural data,[5,9] an X-ray investigation of complexes such as II and III is meaningful. The crystal structure of IIIa was determined from counter data, solved by direct and Fourier methods, and refined by least-squares techniques to $R = 0.07$ for 2726 independent reflections. Crystals are monoclinic, space-group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 9.517$ (4) Å, $b = 15.432$ (14), c 16.915 (8) Å, β 113.17 (6)°.

The crystal structure of IIIa consists of the packing of discrete mononuclear molecules separated by normal van der Waals forces. As may be seen from Figure 1, the molecular structure, which is devoid of any idealized symmetry, may be described in terms of a pseudotetrahedrally coordinated Co atom, by assuming one coordination site for the olefin ligand with mean bond distances Co–P 2.172 (2) Å and Co–C(olefinic) 2.033 (7) Å and mean bond angles P–Co–P 99.4 (4)° and P–Co–B 117.4° (B is the midpoint of the olefinic bond). The significant departure from the ideal tetrahedral value is not surprising as in d^9 complexes Jahn–Teller instability causes distortions away from the most regular structures. The Co(0)–P bond distance is comparable to that of 2.167 Å in $CoH(N_2)(P(C_6H_5)_3)_3$,[11] whereas the agreement with the Co(0)–C distances of 2.06 (1) Å in I is satisfactory.

Viewing down the MA plane, we may also describe the coordination of the cobalt(0)–maleic anhydride complex in terms of a deformed tetragonal pyramid with an apical trimethyl phosphite ligand. However, it is stressed that this formal description would require a difference in apical and basal Co–P bonds, at variance to the observations.

The parameters and bonding of the trimethyl phosphite–cobalt part of the molecule are not significantly different from those observed in trimethyl phosphites,[12] phosphates, or phosphines.[13] In particular, the mean P–O distance of 1.594 (6) Å is close to bond lengths frequently found in tetrahedral organophosphine and orthophosphate esters[13] with P–O–C groupings (average 1.590 Å, range 1.56–1.64 Å) and indicates a certain degree of π bonding. The mean O–C bond length (1.443 (12) Å) is also close to standard (1.44 Å).[13] As usual in these ligands, the M–P–O angles are larger and the O–P–O angles less than tetrahedral; the mean Co–P–O and O–P–O angles are 117.1 and 100.6°, respectively. The latter is close to the standard value (100°).[13] The conformations of the three asymmetric trimethyl phosphite groups with tetrahedrally coordinated pentavalent phosphorous are of the common "two down, one up" arrangement.[12] The orientations of the $P(OCH_3)_3$ groups with respect to the metal do not appear to be influenced appreciably by packing forces.

The most significant structural feature is the conformational change of the maleic anhydride ring in IIIa from the C_{2v} configuration in free maleic anhydride[14] to an idealized C_s configuration in the ligand. The deformation results from the two carbonyl groups bending out of the mean plane of the ring away from the cobalt atom by an average of 0.2 Å. Similar distortions have frequently been observed, as in cyclopentadienyl(duroquinone)-cobalt dihydrate.[15] The mean bond lengths of the ring (C–C 1.435 Å, C=C 1.451 Å, C=O 1.200 Å, C–O 1.418 Å), as compared to those of free maleic anhydride (1.470, 1.303, 1.189, and 1.388 Å, respectively),[14] indicate complete π-electron delocalization. Migration of electrons from cobalt to the olefin may be interpreted as strong back-donation from a d orbital of cobalt to the antibonding π^* orbital of the olefin. This is confirmed by the large decrease of the C=O stretching frequencies from 1780 and 1850 cm^{-1} in free MA to 1722 and 1787 cm^{-1} (Nujol mull) in IIIa. Similar features have been described for other MA complexes.[16-21] The IR spectral evidence confirms that the C=O groups are not directly involved in π coordination because the shifts in ν(C=O) would have been much higher.[22,23] This is also in accordance with the greater mean distance of Co–C(O) as compared to Co–B (see Figure 1).

Our results are in line with the findings of Klein[6] that paramagnetic cobalt(0) compounds with phosphorous ligands are stable and amenable to replacement reactions with retention of the valence state.

Registry No. I, 63372-41-8; II ($R = CH_3$), 82555-92-8; II ($R = C_2H_5$), 82555-93-9; II ($R = CH(CH_3)_2$), 82571-33-3; III ($R = CH_3$), 82555-94-0.

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Iron(III) Phenoxide Complexes: Models for Iron(III)-Tyrosine Coordination

Stephen A. Koch*

Department of Chemistry, State University of New York
Stony Brook, New York 11794

Michelle Millar*

Department of Chemistry, New York University
New York, New York 10003

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The reaction of phenols with $FeCl_3$, which was reported more than a century ago, has remained the classic qualitative test for the hydroxyarene functionality.[1] However, in no instance has the isolation and structural characterization of a Fe(III) complex

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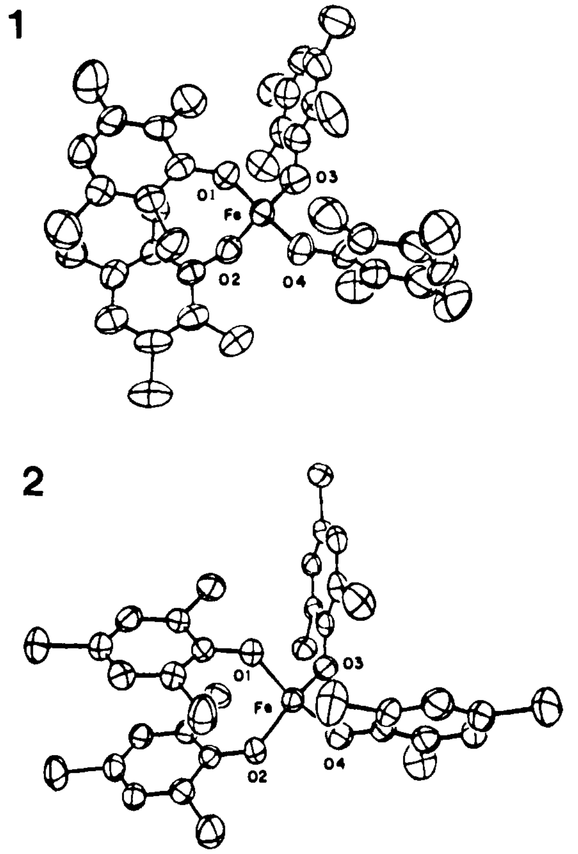

Figure 1. Selected Bond Lengths (Å) and angles (deg). Compound **1**: Fe–O1, 1.826 (4); Fe–O2, 1.861 (4); Fe–O3, 1.852 (4); Fe–O4, 1.847 (4); O1–Fe–O2, 112.5 (2); O1–Fe–O3, 110.8 (2); O1–Fe–O4, 108.5 (2); O2–Fe–O3, 105.9 (2); O2–Fe–O4, 109.6 (2); O3–Fe–O4, 109.6 (2); Fe–O–C (av), 137 (4). Compound **2**: Fe–O1, 1.864 (3); Fe–O2, 1.866 (3); Fe–O3, 1.875 (3); Fe–O4, 1.859 (3); O1–Fe–O2, 107.4 (1); O1–Fe–O3, 105.6 (1); O1–Fe–O4, 122.9 (1); O2–Fe–O3, 116.3 (1); O2–Fe–O4, 99.3 (1); O3–Fe–O4, 105.9 (1); Fe–O–C (av), 134 (4).

with monodentate phenoxide ligands ever been reported. Renewed interest in ferric phenoxide complexes comes from the identification of a large class of metalloproteins that possess the Fe(III)-tyrosine coordination center.[2-5] Herein, we report the syntheses, structures, and properties of two Fe(III) tetraphenolate complexes: [Fe($OC_{10}H_{13}$)$_4$]Et_4N, **1**, and [Fe($OC_6H_2Cl_3$)$_4$]Ph_4P, **2**.

Both **1** and **2** are readily prepared and are isolated as red-orange highly crystalline compounds. The reaction of $FeCl_3$ with lithium 2,3,5,6-tetramethylphenolate and Et_4NBr in ethanol gives **1** in high yield; compound **2** is prepared in an analogous manner with lithium 2,4,6-trichlorophenolate and Ph_4PBr. Both compounds are stable in the solid state but decompose in solution when exposed to water.

The formulation and structure of **1**[6] and **2**[7] have been determined by X-ray diffraction. The average Fe–O distances in the FeO_4 core of **1** and **2** are 1.847 (13) and 1.866 (6) Å, respectively, which are significantly shorter than the average Fe–O distances, 2.02 Å, in the FeO_6 core of [Fe^{III}(catecholate)$_3$]$^{3-}$ compounds.[8,9] The Fe–O–C(Ph) angles for **1** and **2** are similar to those recently reported for an iron(III) complex with a monodentate coordinated catecholate and an iron(III) dimer bridged by a deprotonated hydroquinone.[10] The asymmetric geometry of both complexes is in strong contrast to the high symmetry (S_4 point group) of the analogous 2,3,5,6-tetramethylthiophenolate complex, [Fe($SC_{10}H_{13}$)$_4$][Et_4N], **3**.[11] The Fe–O and C–O distances in **1** and **2** are about 0.4 A shorter than the Fe–S and C–S distances in **3**, which just reflects the difference in the size of an oxygen and a sulfur atom.[12] It is this shortening of these bond lengths that results in a substantial increase in the steric interactions of the ortho-disubstituted ligands and leads to the distortion of the molecules. The FeO_4 core of both anions is distort from tetrahedral symmetry; this distortion is most prominent in **2**, where the O–Fe–O angles vary from 99.3 (1) to 122.9 (1)°. But, in spite of the asymmetric structures of both anions, the observed conformation of the phenolate ligands around the iron appears to be a particularly favorable one, since the conformations are similar in both **1** and **2** (Figure 1).

Table I. Electronic Spectra of $Fe^{III}X_4^-$ Compounds

compd	$\nu_3{}^d$ $(\epsilon)^e$	ν_2	ν_1	Δ_t- $(\nu_2 - \nu_1)^d$
1^a	35 600 (25 900)	31 700 (14 300)	23 700 (9 440)	8000
2^a	34 500 (29 200	30 300 (11 000)	22 900 (9 830)	7400
3^b	33 900 (14 300)	29 100 (6 880)	22 300 (7 230)	6800
$FeCl_4^{-c}$		31 500 (7 600)	27 480 (7 350)	4000

^{a} CH_2Cl_2. ^{b} CH_3CN. ^{c} Reference 14. ^{d} cm^{-1}. ^{e} L mol^{-1} cm^{-1}.

Both **1** and **2** undergo a reversible one-electron reduction at −1.32 and −0.45 V, respectively (vs. SCE; acetonitrile solution). The values of the Fe^{3+}/Fe^{2+} couples reflect the substantial difference in the electron-donating capacities of the ligands. Comparisons of the half-wave potentials of **1** and **3**[11] (which are homologous compounds with FeO_4 and FeS_4 cores), show the Fe^{3+}/Fe^{2+} couple of **1** to be 0.5 V more negative. The Fe-phenolate coordination favors the +3 oxidation state, which is the trend observed for known Fe-tyrosine proteins.[2-5]

As in the case for other Fe(III)-phenolate compounds and proteins,[13] the electronic spectra of **1** and **2** are dominated by intense charge-transfer bands (Table I). With analogy to the assignments of the spectrum of $FeCl_4^-$,[14] the two low-energy bands in **1** and **2** are reasonably assigned as the ligand-to-metal charge-transfer transitions t_1(nb) → e and t_1(nb) → t_2. The low-energy bands of **3** are assigned in a completely analogous manner. The energy separation between these two bands gives the tetrahedral ligand-field splitting parameter Δ_t.[15] The Δ_t values for $FeCl_4^-$ and **1**–**3** predict a spectrochemical series:

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(6) **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.911$ (5) Å, $b = 21.002$ (7) Å, $c = 18.511$ (6) Å, $\beta = 91.40$ (3)°, $V = 4630$ (5) Å, $Z = 4$. The structure was solved by normal methods. The cation has substantial thermal motion and disorder. Anisotropic refinement of the non-hydrogen atoms of the anion and isotropic refinement of the atoms of the cation gave $R = 0.078$ $R_w = 0.11$ using 2850 unique reflections $I > 3\sigma(I)$.

(7) **2** crystallizes in the triclinic space group $P1$ with $a = 13.266$ (2) Å, $b = 13.466$ (2) Å, $c = 15.592$ (2) Å, $\alpha = 113.18$ (1)°, $\beta = 105.78$ (1)°, $\gamma = 90.24$ (1)° $V = 2445$ (2) Å^3, $Z = 2$. The structure was solved by direct methods followed by difference Fourier methods. Final least-squares refinement with anisotropic thermal parameters for the nonhydrogen atoms of the anion and isotropic parameters for atoms of the cation gave $R = 0.043$ and $R_w = 0.068$ using 4683 unique reflections $I > 3\sigma(I)$.

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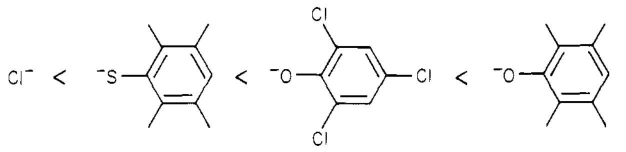

With the exception of catalase,[3] the details of the coordination geometries of the Fe(III)–tyrosine proteins have not been established. None of the known enzymes appears to contain a Fe^{III}-(tyrosine)$_4$ coordination unit. However, the coordination of multiple tyrosines to iron has been indicated in the transferrins,[4] uteroferrin,[16] and the catechol dioxygenases.[17] Further efforts to synthesize models for the Fe–tyrosine proteins are in progress.

Acknowledgment. This work was supported by grants provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of fractional coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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Book Reviews

Advances in Chemical Physics. Volumes 41 and 46. Edited by I. Progogine and S. A. Rice. John Wiley & Sons, Inc., New York. 1981. Volume 41: $60.00. Volume 46: $47.50.

Since its inception many years ago, the "Advances in Chemical Physics" series has maintained admirably high standards in its review of current research developments. Volumes 41 and 46 are welcome additions in this tradition.

Volume 41 begins with a discussion by J. S. Rowlinson of the "penetrable sphere" models for simple fluids which he and Widom first introduced over 10 years ago. Rowlinson presents a current perspective on these ideas after arguing the need for continuous—as opposed to discrete (e.g., "lattice gas")—models for the two-phase fluid equilibrium. Upon reviewing the various exact results and general approximate treatments, the article closes with specific application to the gas–liquid surface. The second contribution is by A. K. Rajagopal, who provides a comprehensive discussion of the density-functional approach to inhomogeneous electron systems, including his original work on extensions of this method to explicitly spin-dependent properties and relativistic systems. Next, F. W. Wiegel and A. J. Knox present a concise review of statistical mechanical theories of lipid monolayers. After commenting on the relevance of these systems to our understanding of the structure and function of real biological membranes, they outline recent progress on exact analyses (in two dimensions, e.g., "dimer" models), numerical simulations, and mean-field theories of the "solid", "liquid", and "gas" phases of the monolayers. The chemical reaction $F + H_2 \rightarrow HF + H$ is discussed next, by J. B. Anderson, as a test ("with more 'character' than $H + H_2 \rightarrow H_2 + H$") of our ability to calculate intermolecular potentials and collision dynamics; the relevant rate measurements and determinations of product state distribution are reviewed as stimuli for these theoretical efforts. Similarly, in an article on radiationless decay processes of small polyatomics in low-temperature solid hosts, V. E. Bondybey and L. E. Brus describe the several experimental techniques which have recently made possible the test of matrix-induced vibrational and electronic relaxation theories for guest molecular species. The theory of excitonic absorption and energy transfer in finite systems ("crystallites") is presented in the following article, by C. Aslangul and P. Kottis. This distinctly formal discussion addresses the fundamental difficulties inherent in treating interacting systems whose properties depend explicitly on the number of sites (i.e., molecules). Finally, S. L. Bernasek reviews new experimental methods for studying elementary chemical reactions which occur on well-characterized solid surfaces.

Volume 46 offers a still more theoretically oriented, and less eclectic, collection of papers. First, L. Frommhold presents a critical discussion of the extent to which ten years of collision-induced ("translational Raman") scattering measurements have allowed us to deduce information about the polarizabilities of interacting pairs of noble gas atoms. The onset of "chaotic" ("irregular", "unstable") motions in nonlinear dynamical systems is discussed next by M. Tabor. His emphasis is on the basic concepts and methods underlying the transition from regular to irregular behavior, rather than on specific applications to real molecular instances of vibrational energy redistribution. R. Kosloff then offers a necessarily abstract discussion of quantum mechanical models for "nonideal" measurements—ones which involve partial resolution and destruction. His article is followed by M. Suzuki's which outlines current theoretical ideas for treating the relaxation of arbitrary unstable states in many-body systems far from equilibrium; general scaling ideas are used to describe the roles of random forces, initial fluctuations, and nonlinearity in controlling the decay of transients. Applications to superradiance and nucleon transport, and extensions of the scaling treatment to multiplicative stochastic processes, are considered. J. S. Rowlinson's paper on the equilibrium properties of the liquid–gas interface (Volume 41) is complemented nicely by the penultimate contribution to Volume 46. Here M. S. Jhon and J. S. Dahler outline the kinetic theory of inhomogeneous fluids, discussing both formal and approximate approaches to the dynamics of the liquid–gas surface. Finally, in a break from the "physicists's systems" treated in all of the above-mentioned articles, A. Ikegami discusses statistical thermodynamic models for the denaturation ("unfolding") of proteins.

William M. Gelbart, *University of California/Los Angeles*

Analytical Chemistry of Polycyclic Aromatic Compounds. By Milton Lee (Brigham Young University), Milos V. Novotry (Indiana University), and Keith D. Bartle (University of Leeds). Academic Press, New York. 1981. xi + 462 pp. $60.00.

In this book the authors present an extensive literature review of the environmental chemistry and analytical chemistry of the polycyclic aromatic compounds (PACs). The compounds considered are the polycyclic aromatic hydrocarbons, the analogues of these in which N, O, or S replace carbon atoms in the fused-ring system, and alkyl-substituted PACs. The primary emphasis of this book is on the analytical chemistry of the PACs. Discussions are organized according to analytical methods which have been proven to be useful. Following a chapter on methods for sample collection and preliminary workup, the applications of the techniques of column, paper, thin-layer, high-performance liquid, and gas chromatographies to PAC analyses are discussed followed by chapters concerning the approaches of mass spectrometry, UV and luminescence spectroscopy, and nuclear magnetic spectroscopy. The book also contains very useful chapters concerning other aspects of the environmental chemistry of the PACs such as their occurrence, toxicology, metabolism, and physical properties.

The general quality of each of the above reviews is excellent. The authors have included an immense quantity of literature while highlighting each subject with well selected, well organized sets of examples. The result is a very readable, yet exhaustive account of the field through 1978. While the book is primarily intended for research chemists involved in PAC environmental effects and analysis, it may also be useful as a course guide for an advanced study in trace organic analysis where the PACs provide a challenging example-set of analyte molecules.

Eric Grimsrud, *Montana State University*

Acute Toxicity in Theory and Practice: With Special Reference to the Toxicology of Pesticides. By V. K. Brown (Shell Research Ltd., Kent). John Wiley and Sons, Chichester, U.K. 1980. ix + 159 pp. $28.00.

Although its title sounds rather technical and academic, this short book reads as easily as an essay or the text of a lecture. It is concerned with toxicity per se rather than toxins and is broadly directed towards students of toxicology, people in scientific administration and regulation, and people associated with pesticide R&D or use. At the outset important terms such as "toxicity", "hazard", and "acute" are defined with clarity and context. The second chapter outlines the types of toxic responses which occur, methods for their quantitative expression, and