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Surface Coordination Chemistry: Corrosion Inhibition by Tetranuclear Cluster Formation of Iron with Salicylaldoxime[**]

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The corrosion of metals represents a waste of both natural resources and money. Corrosion can cause catastrophic accidents because of premature failure of metallic equipment. The world's supply of metals is limited, and wastage due to corrosion leads to consumption of energy and water reserves for producing and fabricating metallic structures. Acorga P5000 (referred to as P50) is a modern corrosion inhibitor for iron and comprises 5-nonylsalicylaldoxime as a mixture of carbon-chain isomers.[1] P50 was developed as an extraction agent for copper,[2] and bis-salicylaldoxime complexes of many dipositive metal ions are known.[3] However, there is no information on the mode of action of P50 on iron surfaces, and data available on iron(II) and iron(III) salicylaldoximate complexes are scant and contradictory.[4–7] We have already identified a variety of bonding modes for salicylaldoxime oligomers with vanadium and zinc.[8] When steel is treated with P50, a purple coating is formed on the surface and constitutes the protective film. Here we describe the iron chemistry of salicylaldoxime and alkyl-substituted analogues and compare the products of these reactions with corresponding materials produced by treating mild steel with these reagents.

Reaction[9] of iron(III) chloride with salicylaldoxime (H_2SalH)[8] led to crystals formulated as $[\{Fe(SalH)(HSalH)\}_4]\cdot H_2SalH\cdot 2\,C_8H_{10}$ (**1**).[10] Compound **1** comprises two molecules of xylene, a molecule of H_2SalH, and a cluster containing four Fe^{III} centers, each of which has a distorted octahedral coordination environment with four O and two *cis*-N donor atoms (Figure 1). Each Fe^{III} center is ligated by a terminal, bidentate HSalH *N*,*O*-donor ligand (those containing N1, N3, N5, and N7 function in this manner) and four atoms (1 N and 3 O) of three of the four bridging SalH ligands (those containing N2, N4, N6, and N8). Each of these bridging ligands joins two Fe^{III} centers through its oximate oxygen atom (μ-O); the attached nitrogen atom links this Fe-O-Fe moiety to a third Fe^{III} center (μ-ON), and the phenolate oxygen atom is bound to this Fe^{III} ion to form a six-membered FeNCCCO chelate ring. The structure of the cluster is further stabilized by four intramolecular hydrogen bonds between a terminal oxime NOH group of the bidentate HSalH ligand and the adjacent phenolate oxygen atom of another such ligand. A similar diversity in the bonding modes of this type of ligand occurs in $[\{VO(SalEt)(HSalEt)\}_2]$.[8]

The four Fe^{III} centers of the tetranuclear cluster of **1** have a distorted tetrahedral arrangement with $Fe\cdots Fe$ distances of about 3.6 Å for linkage by one μ-O and one μ-ON, and about 4.1 Å for linkage by two μ-ON groups. Tetranuclear Fe^{III} clusters, albeit with different structures, were identified in $[Fe^{III}\{Fe^{III}(\text{salicylhydroximato})(MeOH)(\text{acetate})\}_3]\cdot 3\,MeOH$, in which three Fe^{III} centers are arranged about a central Fe^{III} ion,[12a] and $[L_2Fe^{III}_2(\mu_3\text{-}O_2)(\mu_2\text{-}CH_3COO)_3(SalH)_2Fe^{III}_2L_2]X$ (L = 1,4,7-trimethyltriazacyclononane; X = ClO_4, PF_6), the cation of which contains a butterfly arrangement of the four Fe^{III} centers formed by two edge-sharing $Fe^{III}_3(\mu_3\text{-}O)$ triangular units in which deprotonated NO groups bridge the wing and body pairs of iron atoms.[12b]

Elemental analyses, spectroscopic data, and other physical measurements[13] have demonstrated that the predominant constituent of the red-brown product obtained when an Fe salt reacts with salicylaldoxime is the tetranuclear cluster characterized in **1**. The ^{57}Fe Mössbauer isomer shift (0.53 $mm\,s^{-1}$ at 77 K, 0.54 $mm\,s^{-1}$ at 4.2 K) and quadrupole splitting (1.02 $mm\,s^{-1}$ at 77 K, 1.05 $mm\,s^{-1}$ at 4.2 K) are consistent[16–18] with a high-spin Fe^{III} system. The linewidth

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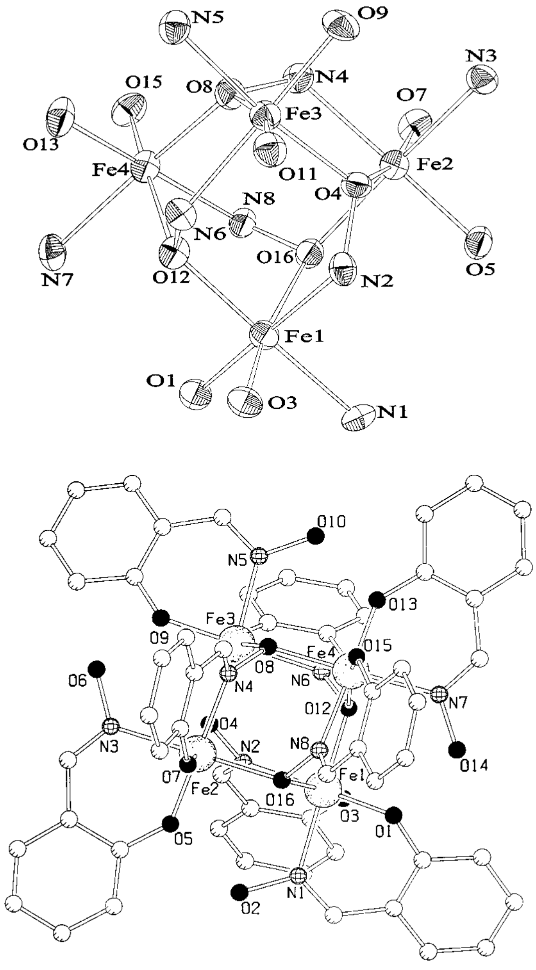

Figure 1. The molecular structure of $[\{Fe(C_7H_6O_2N)(C_7H_5O_2N)\}_4]$. Top: The tetranuclear Fe^{III} cluster showing the coordination sphere of each metal center. Bottom: The overall structure of the cluster viewed down the approximate molecular C_2 (S_4) axis with the H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–O1 1.929(7), Fe1–O3 1.890(8), Fe1–O12 2.041(7), Fe1–O16 2.069(7), Fe1–N1 2.156(9), Fe1–N2 2.113(9), Fe2–O4 2.087(7), Fe2–O5 1.898(7), Fe2–O7 1.900(8), Fe2–O16 2.052(7), Fe2–N3 2.161(9), Fe2–N4 2.120(9), Fe3–O4 2.041(7), Fe3–O8 2.056(7), Fe3–O9 1.925(7), Fe3–O11 1.889(8), Fe3–N5 2.159(9), Fe3–N6 2.137(9), Fe4–O8 2.062(7), Fe4–O12 2.065(7), Fe4–O13 1.924(7) Fe4–O15 1.887(8), Fe4–N7 2.155(9), Fe4–N8 2.135(9); N1-Fe1-O1 84.7(3), N2-Fe1-O3 84.7(4), O1-Fe1-O12 91.7(3), O1-Fe1-O16 95.8(3), N3-Fe2-O5 85.6(3), N4-Fe2-O7 84.4(3), O5-Fe2-O7 92.7(3), O5-Fe2-O16 91.6(3) N5-Fe3-O9 84.5(4), O8-Fe3-N6 81.4(3), O11-Fe3-N6 84.4(4), N6-Fe3-O4 90.5(3), N7-Fe4-O13 85.8(4), O12-Fe4-O8 85.2(3), N8-Fe4-O15 83.6(3), N7-Fe4-O12 85.5(3); Fe···Fe distances [Å]: Fe1–Fe4 3.547(3), Fe1–Fe2 3.607(3), Fe1–Fe3 4.050(2), Fe2–Fe3 3.568(3), Fe2–Fe4 4.068(3), Fe3–Fe4 3.603(3).

(0.38 mm s^{-1} at 77 K, 0.66 mm s^{-1} at 4.2 K) and the appearance of a magnetic pattern at 1.5 K with an overall splitting of 4.7 T are consistent with the presence of a small cluster.[14–16] In aqueous, aerobic media, the same product is obtained irrespective of whether an iron(II) or an iron(III) salt is used as starting material. 5-*tert*-Butyl- and 5-(1,1,3,3-tetramethylbutyl)salicylaldoxime (which are close analogues of P50) react with Fe^{II} or Fe^{III} salts to produce dark purple precipitates that were shown by spectroscopy to contain a tetranuclear Fe^{III} core analogous to that in **1**. Whilst freshly precipitated $Fe(OH)_2$ or $Fe(OH)_3$ yielded such products, aged samples of these hydroxides, as well as α-FeOOH,[17] α-Fe_2O_3,[17] γ-FeOOH,[18] β-FeOOH,[19] and rust (produced by the exposure of a Q panel[20] to the Manchester environment for one month) showed no reaction with salicylaldoxime or its alkyl-substituted derivatives.

Degreased Q panels were treated with 1M H_2SO_4 for 30 s, washed with distilled water, and treated, by spinning, with an alcoholic solution of salicylaldoxime. Scanning electron micrographs showed the formation of a thick surface layer. The Fe(2p), Fe(3p), O(1s), and N(1s) X-ray photoelectron spectra (XPS) of the treated panels were identical to those of the isolated tetranuclear cluster. Therefore, the differences between the O(1s) and N(1s) XPS chemical shifts of the treated panels and the free ligands are particularly significant. Similarly, the dominant features in the attenuated total reflection FT-IR spectrum of the treated panels closely resembled those of the isolated tetranuclear cluster. Extraction of the surface coating allowed analytical and further spectroscopic investigations to be accomplished. Elemental analyses, mass spectrometric, EPR, FT-IR, XPS, UV/Vis absorption, and magnetic susceptibility measurements were all consistent with the presence in the surface coating of a high proportion of the tetranuclear cluster identified in **1**. The Fe K-edge X-ray absorption spectra of the isolated tetranuclear cluster and the solid extracted from the surface coating were essentially identical. The energy of each of the K absorption edges is consistent with the presence of Fe^{III}.[21] The Fe K-edge EXAFS spectra of the surface coating and **1** are each well described by backscattering contributions from shells of light atoms at 1.93, 2.10, 2.91, and 3.06 Å (assigned as 4 O, 2 N, 4 C, and 4 C, respectively), consistent with the crystal structure of **1**. Although Fe K-edge EXAFS provided no clear evidence for the proximity of Fe atoms, this is not unexpected, given the spread in the crystallographically determined Fe···Fe distances (3.547(3) – 4.068(3) Å). When 5-*tert*-butyl or 5-(1,1,3,3-tetramethylbutyl)salicylaldoxime was used, the spectroscopic properties of the surface product were also consistent with the formation of compounds structurally analogous to the tetranuclear cluster of **1**.

Therefore, we postulate that the corrosion inhibition by P50 on an iron surface is due to the generation of a tetranuclear cluster complex.[22] Iron ions must be available for the formation of such species, and the efficiency of P50 is therefore enhanced by treatment of an oxidized iron surface with a mild acid. The results reported here provide evidence, in addition to the information obtained on the nature of the interaction of oxidized Cu surfaces with benzotriazole,[23] that corrosion inhibition at a metal surface can involve the production of metal clusters. The low ligand/metal ratio which arises for a ligand in immediate contact with an oxidized metal surface means that polyfunctional ligands have advantages over monofunctional ligands as corrosion inhibitors. Polyfunctional ligands tend to produce compact polymetallic assemblies and, when formed at the surface of a metal, such species can form a protective barrier which inhibits corrosion.

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[8] For salicylaldoximates(1 −) (= HSalR) and for salicylaldoximates-(2 −) (= SalR) we have crystallographically characterized several compounds, including [{VO(SalEt)(HSalEt)}$_2$], in which i) HSalEt acts as a terminal chelator; ii) SalEt forms μ-NO bridges between the two metal atoms and chelates to one of them through the phenolate group; and iii) two hydrogen bonds are formed, each of which involves a protonated oxime O atom of an HSalEt ligand and the phenolate O atom of the adjacent SalEt group; R. L. Beddoes, D. Collison, C. D. Garner, J. Grigg, M. Helliwell, P. A. Tasker, D. Thorp, J. M. Thorpe, unpublished results.

[9] An aqueous solution of iron(III) chloride was treated with salicylaldoxime in EtOH and neutralized with one equivalent of base to give a red-brown precipitate. Washing this product with hexane removed excess ligand, and subsequent extraction with CH$_2$Cl$_2$ followed by solvent evaporation in vacuo yielded a dark brown solid. Slow evaporation at room temperature of a solution of this solid in xylene gave black platelike crystals suitable for X-ray diffraction.[10]

[10] The crystal and molecular structure of a crystal of dimensions 0.03 × 0.2 × 0.45 mm was determined on a Rigaku AFC5R diffractometer with graphite-monochromated Cu$_{K\alpha}$ radiation ($\lambda = 1.54178$ Å, $\mu = 67.04$ cm^{-1}) and a 12-kW rotating anode generator at room temperature. $C_{79}H_{71}N_9O_{18}Fe_4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.136(2)$, $b = 21.815(6)$, $c = 12.828(2)$ Å, $\alpha = 97.64(2)$, $\beta = 105.65(1)$, $\gamma = 84.95(2)^\circ$, $V = 3770(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.460$ g cm^{-3}, $F(000) = 1712$. The scan was of the $\omega/2\theta$ type with a scan rate of 8.0° min^{-1}. Of the total of 11210 unique reflections collected with $2\theta_{max} = 120.3^\circ$, 4851 with $I > 3\sigma(I)$ were used for structure determination by direct methods.[11] An absorption correction using the program DIFABs was applied to the data (N. P. C. Walker, D. I. Stuart, *Acta Crystallogr. Sect. A* **1983**, *39*, 158–166). Full-matrix least-squares refinement with anomalous dispersion for all non-hydrogen atoms gave residuals of $R = 0.068$ and $R_w = 0.069$, where $R = \Sigma|\Delta|/\Sigma|F_o|$ and $R_w = (\Sigma\Delta^2/\Sigma wF_o^2)^{1/2}$, $\omega = 1/[\sigma^2(F_o) + 0.00022\,|F_o|^2]$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103013. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[13] The IR spectrum of **1**, as an evaporated thin film or KBr disk, shows a rich, well-resolved fingerprint between 2000 and 250 cm^{-1}, typical of a salicylaldoxime complex. The UV/Vis absorption spectrum ($\lambda_{max}(\varepsilon)$ = 310 (34000), 514 nm (8000 M^{-1} cm^{-1})), EPR powder spectrum ($g \approx 2$, $\Delta B_{p-p} = 1500$ G for Q band), magnetic susceptibility in CHCl$_3$ by the Evans NMR method (5.2 μ_B per iron atom at 235 K) and mass spectrum (positive-ion FAB, m/z: 1308.5, 1172, 1035, 900 for $[\mathrm{Fe_4(C_7H_6O_2N)}_n\mathrm{(C_7H_5O_2N)_4}]^+$ with $n = 4$, 3, 2, and 1, respectively) are consistent with and diagnostic of the structure of the tetranuclear cluster.

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[20] A Q panel is a small, rectangular piece of mild steel of reproducible composition and surface texture used to test the corrosion inhibition properties of organic molecules.

[21] The Fe K-edge position of the surface product and the isolated tetranuclear cluster were measured as 7127 eV with a pre-edge feature at 7113 eV, and essentially identical values were obtained for hematite (α-Fe$_2$O$_3$). These values were referenced to the Fe K-edge energy of an iron foil at 7112 eV.

[22] Although all of our experimental evidence points to the formation of a tetranuclear iron cluster, we note that other nuclearities are possible, for example, a trinuclear assembly formed with a functionalized derivative of salicylaldoxime, as described by E. Bill, C. Krebs, M. Winter, M. Gerdan, A. X. Trautwein, U. Flörke, H.-J. Haupt, and P. Chaudhuri, *Chem. Eur. J.* **1997**, *3*, 193–201.

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Stereoselective Solid-Phase Synthesis of β-Lactams—A Novel Cyclization/Cleavage Step towards 1-Oxacephams**

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The solid-phase method is an extremely efficient approach for the synthesis of small molecules.[1] A current trend is to extend the principles of organic reactions that take place in homogenous phase to analogous reactions that take place on solid supports. To date, the syntheses of a variety of classes of heterocycles by solid-phase synthesis methodology have been reported.[1] However the solid-phase synthesis of β-lactams, though attractive structures because of their antibiotic activity, have been barely reported.[2] Herein we describe new resin-based chemistry for the straightforward construction of 1-oxacephams, which represent a class of compounds with potential biological activity.[3] The development of new

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