Iron(III) Di(2-ethylhexyl)phosphate Complexes: Ligand Control of Co-ordination Polymerization

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A novel dinuclear complex comprised of H^+/NO_3^- bridged tris[di(2-ethylhexyl)phosphate]iron(III) units, $Fe(dehp)_3$, having the molecular formula $[Fe_2(dehp)_5(Hdehp)(NO_3)]$, is described which surprisingly is colourless, stable under ambient conditions, and highly soluble in cyclohexane. Solution reaction with water leads to replacement of H^+/NO_3^- by H_2O producing a highly insoluble polymer having molecular formula $[\{Fe(dehp)_3(H_2O)\}_n]$. Interconversion between the contrasting polymeric and dinuclear species is facile and represents an example of reversible co-ordination polymerization–depolymerization with the two species differing remarkably in their properties. The preparation, characterization, and interconversion of these iron complexes are described.

Di(2-ethylhexyl)phosphoric acid, Hdehp, is one of the most commonly used phosphate ligands in the study of liquid–liquid extraction processes.[1–8] It has been reported that Hdehp forms complexes of unusual stoichiometries with transition metals, the most frequently encountered being $[M(dehp)_3(Hdehp)_3]$,[8–10] and $M_x(dehp)_y(Hdehp)_3$,[9–11] but $[M(NO_3)(dehp)_3]$ (M = Hf or Th) and $[\{MO_{0.5}(NO_3)(dehp)_2\}_n]$ (M = Zr or Ce) polymers have also been reported.[4] In general, these complexes have been obtained by the extraction of the metal ion into organic solvents from aqueous solutions. More usual stoichiometries, $M(dehp)_x$, result from stoichiometric reaction of the metal salts with the sodium or potassium salts[3,12] of $dehp^-$.

This report summarizes the preparation and properties of a unique dinuclear complex having the composition $[Fe_2(dehp)_5(Hdehp)(NO_3)]$, and the related polymeric hydrate $[\{Fe(dehp)_3(H_2O)\}_n]$; they are prepared and isolated directly from organic and aqueous solvents, respectively. The complex $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ is a most interesting and unusual compound of good stability that is readily obtained in high yield. Its novel structure involves bridging by both H^+ and NO_3^-, and despite its peculiar stoichiometry, it is not obtained by solvent extraction. Further unusual properties are its unexpected film-forming tendency and its high solubility in solvents of low polarity, from which it is readily isolated in good yield. In contrast, the hydrated complex, $[\{Fe(dehp)_3(H_2O)\}_n]$ is an insoluble, rubbery powder. Despite the great differences in the properties of the complexes, the water-stable, well behaved complex $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ can be prepared directly from the intractable species $[\{Fe(dehp)_3(H_2O)\}_n]$ *via* dehydration and acidification. This reversible transformation constitutes facile interconversion between a polymer and a dinuclear species.

Experimental

Reagent grade hydrated iron(III) nitrate was used as received, Hdehp was obtained from Albright & Wilson or Aldrich and its purity was established by ^{31}P NMR spectroscopy. Ultrapure water was used for ion chromatography. Glacial acetic acid was reagent grade and used without further purification.

Synthesis of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$.—This preparation can be carried out in a variety of organic solvents, but is best accomplished in glacial acetic acid. With vigorous stirring, Hdehp (9.96 g, 31.0 mmol) in acetic acid (15 cm^3) was added dropwise to $Fe(NO_3)_3{\cdot}9H_2O$ (4.01 g, 9.92 mmol) in acetic acid (35 cm^3). The rust-red solution rapidly deposited solids as it lightened in colour to yellow. Upon complete addition of the ligand the mixture became completely white. The solid was collected, dispersed in acetic acid (15 cm^3), stirred, filtered off and vacuum dried at room temperature to constant weight (8.6 g, 82%). Recrystallization may be accomplished by dissolving in a minimum amount of cyclohexane containing a small amount of acetone, followed by precipitation with acetone. A colourless waxy solid is obtained in this way, and about half of the product remains in the pale yellow mother-liquor. Viscous solutions containing approximately 30% by weight of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ in cyclohexane can be prepared. The complex forms a clear, non-self supporting film when allowed to dry from solution. Attempts to obtain X-ray quality crystals by recrystallization, slow evaporation or slow diffusion techniques were not successful; amorphous, waxy solids were always obtained.

Synthesis of $[\{Fe(dehp)_3(H_2O)\}_n]$.—The preparation of $[\{Fe(dehp)_3(H_2O)\}_n]$ was carried out by rapid dropwise addition of a solution of Hdehp (32.0 g, 99.4 mmol) and KOH [6.0 g, 105 mmol in water (500 cm^3)] to a mechanically stirred solution of $Fe(NO_3)_3{\cdot}9H_2O$ (12.0 g, 29.7 mmol) in water (500 cm^3). After filtration the solid was again dispersed in water, refiltered and air-dried overnight. Vacuum-drying to constant weight at room temperature yielded a colourless, rubbery solid in high yield. This complex exhibits only low solubility in organic solvents; the small fraction that does dissolve yields pale yellow solutions. Carrying out the same aqueous procedure, but with iron(III) sulfate, provided a complex which has similar low solubility in organic solvents, including cyclohexane, in contrast to the previously reported product of a procedure that appears to be similar.[13] Iron(III) chloride yielded a yellow product, presumably containing Fe–Cl–Fe bridged species.

Interconversion.—The complex $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ can be obtained directly from $[\{Fe(dehp)_3(H_2O)\}_n]$. Dissolving

$[\{Fe(dehp)_3(H_2O)\}_n]$ in refluxing triethyl orthoformate yields a clear solution, depending upon concentration, from which $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ is precipitated by adding HNO_3, followed by water or acetone. The addition of water alone (in the absence of acid) causes the reprecipitation of $[\{Fe(dehp)_3(H_2O)\}_n]$. Our attempts at obtaining X-ray quality crystals of either composition by slow evaporation or slow diffusion of a non-polar solvent into the triethyl orthoformate solution were not successful.

Instrumental and Analytical Techniques.—Differential scanning calorimetry analyses were run at 10 °C min^{-1} on a DuPont model 912 dual sample differential scanning calorimeter (closed pan), controlled by a DuPont Instruments 9900 computer/thermal analyser. Samples were run under nitrogen purge (50 cm^3 min^{-1}): calibration was accomplished with pure indium. Hi-Res™ thermal gravimetry samples were run on a TA Instruments model TGA 2950 thermographic analyser under the following conditions: 50 °C min^{-1} heating rate, High Res Scan resolution = 4, sensitivity = 2, nitrogen purge at 100 cm^3 min^{-1} (10–14 mg sample sizes).

Elemental analyses were carried out in the 3M Analytical Services group. ^{31}P NMR spectra were recorded on a Varian XL-400 spectrometer at 161.9 MHz using a 5 mm probe and standard data acquisition techniques. The solution magnetic susceptibility of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ was determined in cyclohexane by the Evans technique[14] and corroborated *via* the Ward method,[15] including Orrell and Sik corrections,[16] on a Varian XL-100 NMR spectrometer at ambient temperature (30 °C).

Ion chromatography was carried out on a Waters IC-PAK™ Anion Guard-PAK™ column (5 cm × 4.6 mm internal diameter) at 1.2 cm^3 min^{-1}, in a Hewlett-Packard 1090 chromatograph with a Waters model 430 conductivity detector. The mobile phase was comprised of 1.1 mmol dm^{-3} gluconic acid, 8.2 mmol dm^{-3} boric acid [prepared from a concentrate of boric acid (17.0 g, 275 mmol), purified gluconic acid (11.8 cm^3 of a 50% solution), $LiOH{\cdot}H_2O$ (4.3 g, 102 mmol) and glycerine (62.5 cm^3) diluted to 500 cm^3] and 12% acetonitrile. Samples of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ were dissolved in cyclohexane and extracted with water. Calibration was accomplished with sodium nitrate.

Samples for IR spectra were recorded using KBr sample techniques on a Perkin Elmer 983 spectrophotometer under ambient conditions. Raman spectra were recorded on a Spex Ramalog 1401 spectrometer with an RCA photomultiplier having a cooled, broad-response doped gallium arsenide photocathode. A Spex amplifier/discriminator was used to feed pulses to a Nicolet 1180 computer equipped with signal averaging software. A Lexel argon-ion laser was operated at 5145.5 Å.

Mass spectra were obtained with a Kratos MS-50 triple analyser using a standard Kratos fast atom bombardment (FAB) source equipped with an Ion Techatom gun. Samples in glycerol or triethanolamine were bombarded with 8 keV (*ca.* 1.28 × 10^{-15} J) xenon atoms on the copper target of the FAB direct insertion probe. The ions produced were accelerated through 8 keV into the analyser region of the mass spectrometer.

The TGA–MS–IR measurements were recorded on a coupled apparatus comprising an Omnitherm TGA 1500, Hewlett-Packard 5988 GC/MS and a Bio-Rad Digilab FTS-45. The units were coupled by a heated (200 °C) silica-lined stainless steel capillary which fed a 20 m, 0.15 mm internal diameter glass capillary (open split) connecting the mass spectrometer in place of the GC–MS inlet system. The entire glass capillary was fitted inside the GC oven and kept at 200 °C. Sampling gas flow rates were maintained at 4–5 cm^3 min^{-1}.

Results

Elemental analysis clearly establishes the fundamental compositions. In the case of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$, elemental analysis for five elements is in excellent agreement with the proposed 2:1 Fe:NO_3 ratio. In addition, ion chromatography both clearly confirms the presence of nitrate and quantitatively agrees with the elemental analysis for nitrogen content (Found: C, 54.6; H, 9.6; Fe, 5.8; N, 0.7;* P, 8.9. $C_{96}H_{205}Fe_2NO_{27}P_6$ requires C, 54.85; H, 9.8; Fe, 5.3; N, 0.7; P, 8.85%). For $[\{Fe(dehp)_3(H_2O)\}_n]$ the analysis is in excellent agreement for five elements (Found: C, 55.5; H, 10.0; Fe, 5.1; N, 0.1; P, 8.95. $C_{48}H_{104}FeNO_{13}P_3$ requires C, 55.5; H, 10.1; Fe, 5.4; N, 0.0; P, 8.95%). The result for N analysis of 0.1% is within the experimental error, but considering the insolubility of the complex, a small amount of occluded NO_3^- would not be surprising.

Differential scanning calorimetry and Hi-Res™ TGA scans for the iron complexes are shown in Fig. 1. The DSC scan for $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ reveals that the complex is thermally stable up to 100 °C, beyond which a complicated, irreversible endothermic transition, centred at about 125 °C, occurs. This is followed by a second endothermic transition centred at about 185 °C. The main endothermic decomposition occurs at 290 °C. Standard TGA techniques yielded unresolvable weight losses spanning the 150–300 °C temperature range.

The Hi-Res™ TGA shows the first weight loss, centred at 216.8 °C amounting to 302 amu {based on $[Fe_2(dehp)_5(Hdehp)(NO_3)]$}. This is reasonable for the loss of one mole of 2-ethylhexan-1-ol (130 amu) per iron. Infrared and MS analysis of the first volatile decomposition products from the TGA scan confirmed that this loss is due to 2-ethylhexan-1-ol. The source of the second weight loss (239 °C, 105 amu) is clearly loss of HNO_3 (63) which, as can be seen in the data, most likely includes the initial onset of loss of organic materials. Olefinic cleavage, such as that observed for other metal organophosphate systems,[17] is observed to begin after the 2-ethylhexan-1-ol peak. The final weight loss at 257.1 °C amounts to 50.58%, corresponding to the theoretical loss of all organic matter leaving $Fe(PO_3)_3$ (Found: 28.3. Expected: 27.8%).

The DSC of $[\{Fe(dehp)_3(H_2O)\}_n]$ shows a complicated endothermic transition starting as low as 130 °C which, by direct examination, appears reproducibly to form a partial melt. The primary decomposition endotherm is centred at 299 °C. The primary weight loss transition seen in the Hi-Res™ TGA is centred at 221.6 °C, very similar to that found for the $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ complex. Its weight loss (133 amu) corresponds very closely to 2-ethylhexan-1-ol (130 amu). Infrared and MS analysis of the first volatile decomposition products from the TGA confirmed that this loss is due to 2-ethylhexan-1-ol. The remaining weight loss, centred at 255.9 °C is also very similar to that for the $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ complex. Furthermore, the residue of 27.4% is reasonable for the formation of $Fe(PO_3)_3$ (28.2%).

The fact that pyrolysis of both compounds leads to the same terminal product $Fe(PO_3)_3$ is consistent with the expectation that the loss of HNO_3 from the dinuclear species and the loss of water from the polymer should produce related polymeric intermediates. This is also supported by the occurrence of both processes within a common temperature range centred at 256–257 °C.

The infrared spectrum of the nitrate complex, Fig. 2, exhibits key NO_3^- absorptions at 1550 and 1262 cm^{-1} (the N–O stretch expected at 1010 cm^{-1} is buried under bands arising from dehp). This is consistent with the binding of nitrate through two of its oxygen atoms, either as a result of bidentate chelation or of bridging.[18,19]

Similar spectra have been reported for a group of $M(NO_3)_x(dehp)_y$ complexes, where M = Zr, Hf, Th or Ce.[4] Preparation of the zirconium complex in this laboratory produced a material whose IR spectrum was found to be very similar to that of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$, with the ex-

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* From ion chromatography; combustion analysis gave 0.4 ± 0.3%.

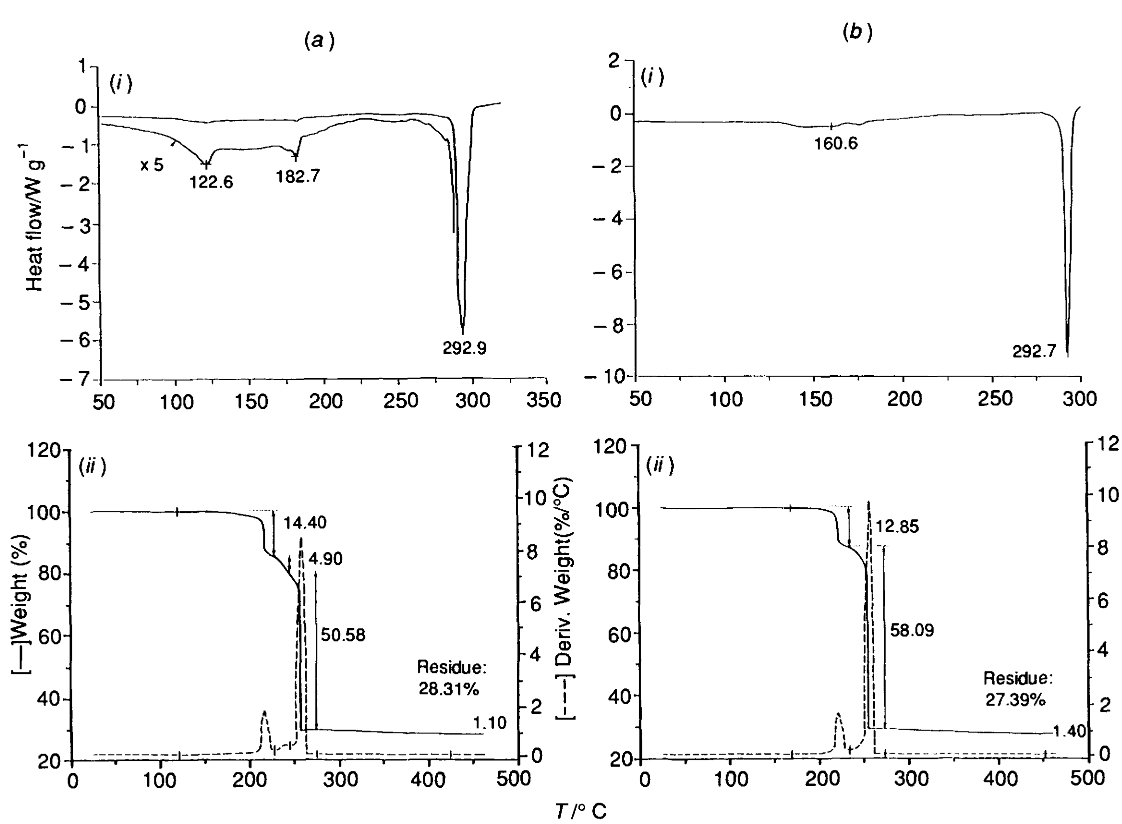

Fig. 1 DSC (*i*) and Hi-Res™ TGA (*ii*) scans of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ (*a*) and of $[\{Fe(dehp)_3(H_2O)\}_n]$ (*b*)

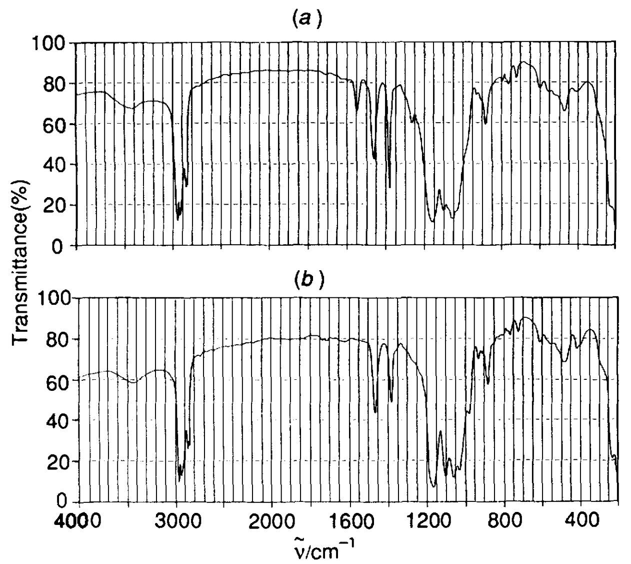

Fig. 2 Infrared spectra of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ (*a*) and of $[\{Fe(dehp)_3(H_2O)\}_n]$ (*b*)

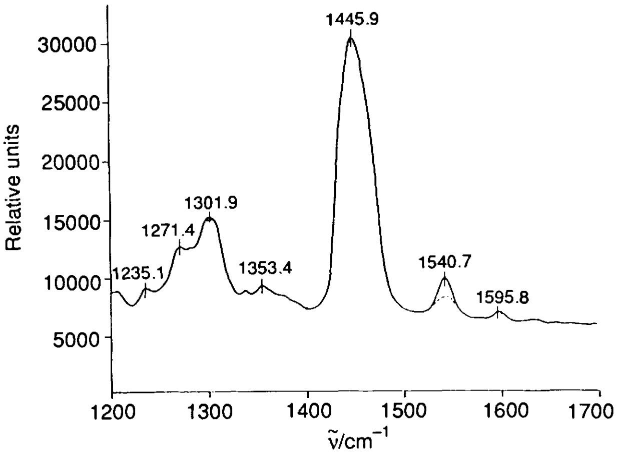

Fig. 3 Polarized Raman spectra of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$, (– – – –) perpendicular polarization

pected asymmetric and symmetric nitrate stretches also at 1550 and 1262 cm^{-1}, respectively. Infrared spectra of other metal nitrate complexes demonstrate that $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ contains NO_3^- which, on that basis alone, is not unidentate or ionic but could be either bidentate or bridging, since ν_5, ν_1 and $\nu_5 - \nu_1$ are all in the same range[20] for these two types of NO_3^- co-ordination.

The IR spectrum of $[\{Fe(dehp)_3(H_2O)\}_n]$ is, with the exception of the two nitrate bands, very similar to that of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$. The similarity would be expected for complexes containing the same basic $\{Fe(dehp)_3\}$ units and related co-ordination spheres.

The polarization of the nitrate bands in the Raman spectra can be used to differentiate between the monodentate and bifunctional co-ordination (chelation and bridging) of the nitrate in metal complexes.[18,19] The polarized Raman spectra of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ are displayed in Fig. 3. Except for the 1540.7 cm^{-1} band, all of the absorptions between 1200 and 1700 cm^{-1} are identical for the two polarizations. This observation that the 1540.7 cm^{-1} nitrate absorption is polarized while the 1271.4 cm^{-1} nitrate absorption is depolarized demonstrates that the nitrate is co-ordinated through two oxygen atoms as in a bridge.

Molecular-weight determination of the organic-soluble nitrate derivative by gel-permeation chromatography was not successful and low-angle light scattering, in cyclohexane, revealed the molecular weight to be less than 3000, the lower molecular-weight limit of this technique. Mass spectral determinations on both complexes by fast atom bombardment (FAB) revealed no ions of mass greater than 1019 and 1021 by

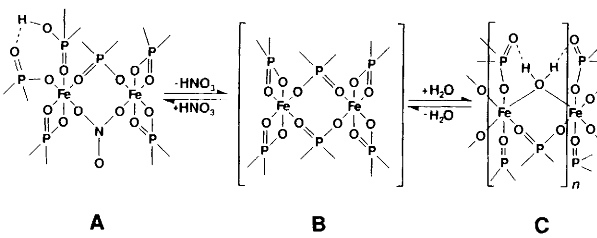

Fig. 4

negative-ion bombardment. No higher mass unit ions were seen out to 9500, the maximum expected for a $[Fe(dehp)_3]_{10}$ species[2] [the monomeric unit $Fe(dehp)_3$ has a mass of 1020]. From these results it can be concluded that there is no evidence for polymerization in the case of the nitrate derivative. Further, the results are all consistent with the existence of a weakly bridged dinuclear $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ species.

Solid-state ^{31}P NMR spectroscopy on these two complexes demonstrated significant differences between them. For $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ no phosphorus signal was detectable, due to paramagnetic line broadening caused by the iron. For $[\{Fe(dehp)_3(H_2O)\}_n]$, on the other hand, a strong signal at δ 2 (relative to phosphoric acid) was easily observed.

The magnetic susceptibility of $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ was determined in cyclohexane solution by NMR measurements, and a value of $\chi_m = 13.8 \times 10^{-6}$ was obtained, giving a magnetic moment μ_{eff} of 5.84 per Fe. This value is in the normal range for high-spin Fe^{3+} complexes and is also consistent with only weak bridging between the two iron centres in the dinuclear species.

Discussion

The detailed chemical and physical properties of the new compounds must be interpreted in light of the fact that acidic diorganophosphorus ligands are known primarily to co-ordinate metal ions by bridging between metal centres.[2,4,7,10,21–25] On the basis of the contrasting properties of the iron organophosphate complexes, the $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ and $[\{Fe(dehp)_3(H_2O)\}_n]$ complexes may be described as representing departures in opposite directions from a common parent, a proposed dimeric species of the simple composition $[\{Fe(dehp)_3\}_2]$. Evidence for such a species was found in the IR and thermal analysis studies summarized above and is also consistent with the solubility of this intermediate during interconversion of the $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ complex to the $[\{Fe(dehp)_3(H_2O)\}_n]$ complex. Therefore, the presumed parent compound is expected to contain a pair of bridging phosphates; triple bridges are possible but not expected with such bulky ligands as dehp. A rational structure for this parent species is shown as structure **B** in Fig. 4.

The opposite relationships for the two new compounds are emphasized by the remainder of Fig. 4. The H^+/NO_3^- adduct, a dinuclear $[Fe_2(dehp)_5(Hdehp)(NO_3)]$ complex, depicted as structure **A**, is consistent with all of the data discussed above, including physical properties. One of the bridging phosphates in the parent complex has been replaced by a bridging nitrate which is expected for a complex exhibiting no substantial coupling as revealed by magnetic measurements on this compound. In addition, the polarized Raman data further confirm the characterization of the nitrate as bridging. Despite previous proposals for the disposition of the proton in such a structure,[8,13] a definitive precedent only recently has been reported for the complex $[Mn(O_2PPh_2)(HO_2PPh_2)(dmf)_2]$ (dmf = dimethylformamide) which has been characterized by an X-ray crystal-structure determination.[26] This established the presence of a $-P{=}O \cdots H{-}O{-}P-$ chelate ring which is also proposed in our system. This indirect evidence is especially important since the waxy nature of $[Fe_2(dehp)_5)(Hdehp)(NO_3)]$ effectively eliminates the possibility of obtaining an X-ray structure determination on this compound.

The $[\{Fe(dehp)_3(H_2O)\}_n]$ complex can be constructed from the same parent in a similar manner. A highly polymeric structure accounts for its very low to vanishingly small solubility in all solvents examined. Further, its diamagnetic character suggests relatively short and strong bridging linkages between adjacent iron(III) centres which cannot be accounted for simply by short Fe–O(P)–Fe bridging links even though these links are known to produce weak antiferromagnetic coupling.[25,27] The need to account for the diamagnetic property of this complex, the known $-P{=}O \cdots H{-}O{-}P-$ chelate ring, and the remaining data all argue for the formation of the polymer whose structure is proposed to be **C** (Fig. 4). The structure indicated is consistent with all of the results presented above. Thus the hydrate of the parent $\{Fe(dehp)_3\}_n$ is a polymer containing bridging water molecules, and the strong $Fe{-}O(H_2){-}Fe$ bridge explains the magnetic results. The absence of colour also argues for an unusual bridging moiety since commonly oxo- and hydroxo-bridged iron species invariably display substantial colour attributable to ligand-to-metal charge-transfer transitions. It is suggested that the proposed hydrogen bonding to a bridging water molecule facilitates the reported antiferromagnetic coupling while suppressing the usual charge-transfer transitions. The two iron compounds, while having contrasting physical and chemical properties, share distinctive features, a phosphate bridged structure and a $-P{=}O \cdots H{-}O{-}P-$ chelate ring which is adequate to stabilize the bridged species.

In both of these complexes, the $Fe(dehp)_3$ monomeric unit is the basic building block. The conversion of one complex into the other is accomplished simply by altering the available bridging species and changing the strength of the acid in the medium. In both cases proton binding sites are provided by incorporating the proton into new, hydrogen-bonded chelate rings created by binding it to two previously monodentate phosphate ligands. Dehydration followed by acidification converts $[\{Fe(dehp)_3(H_2O)\}_n]$ into $[Fe_2(dehp)_5(Hdehp)(NO_3)]$; effectively, the $-P{=}O \cdots H{-}O{-}P-$ unit is freed upon dehydration of $[\{Fe(dehp)_3(H_2O)\}_n]$ and it then accepts the proton of HNO_3 as the nitrate ion replaces a bridging phosphate. The opposite reaction is driven by formation of the thermodynamically more stable $Fe{-}O(H_2){-}Fe$ bridges.

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