Preparation, Properties, and X-Ray Crystal Structure of Tris(O,O'-di-isopropyl phosphorodithioato)iron(III), [Fe{S₂P(OPrⁱ)₂}₃]. Comparison of Structure and Bonding in Phosphorodithioato- and Dithiocarbamato-complexes†

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The title compound [Fe{S₂P(OPrⁱ)₂}₃] has been prepared by a method which gives a stable product. The structure, determined by single-crystal X-ray diffraction, is distorted octahedral. The iron(III) is high-spin. The i.r., u.v.–visible, and e.s.r. spectra are reported. For complexes [ML₃] (L = phosphorodithioate or dithiocarbamate) distortions from octahedral geometry, metal–sulphur bond lengths, and covalent contributions to the metal–sulphur bond are discussed.

We report the preparation, u.v.–visible, i.r., and electron spin resonance spectra, magnetic properties and single-crystal X-ray structure of the compound tris(O,O'-di-isopropyl phosphorodithioato)iron(III), [Fe{S₂P(OPrⁱ)₂}₃]. The compound was prepared during our research on metal complexes in lubricating oils.[1] Formulated oils contain a number of additives including phosphorodithioato-complexes of, usually, zinc or molybdenum. The phosphorodithioates reduce friction and wear between sliding surfaces and act as antioxidants. It is possible that iron or iron(III) oxide might react with phosphorodithioates in a lubricating oil to form a phosphorodithioate of iron. Our aim was to prepare an authentic iron(III) phosphorodithioate, and to determine its structure and characteristic properties as a basis for determining whether iron phosphorodithioates were present, or formed, in lubricating oils. Hitherto iron phosphorodithioates have been thought of as unstable, decomposing quickly to intractable sticky solids.[2] We have now prepared and characterised a stable iron(III) phosphorodithioate. It is a high-spin iron(III) complex with a distorted octahedral structure.

Experimental

Preparation of Tris(O,O'-di-isopropyl phosphorodithioato)-iron(III), [Fe{S₂P(OPrⁱ)₂}₃].—Di-isopropyl phosphorodithioic acid (12.5 g) was added to a suspension of iron(III) oxide, Fe₂O₃ (1.6 g), in n-heptane (50 cm³). The mixture was stirred and heated at 60 °C for 0.5 h. Unreacted Fe₂O₃ was filtered off. The filtrate on leaving deposited black crystals of the required compound. The black crystals were filtered off and washed with methanol. Yield: 8.67 g (64.0%) (Found: C, 30.3; H, 5.85; P, 12.9; S, 24.5. Calc. for C₁₈H₄₂FeO₆P₃S₆: C, 31.1; H, 6.05; P, 11.9; S, 24.6%). A similar product was obtained from iron powder and di-isobutylphosphorodithioic acid.

Spectroscopic Measurements.—U.v.–visible spectra of solutions of [Fe{S₂P(OPrⁱ)₂}₃] in toluene and dichloromethane were recorded on a Unicam SP spectrophotometer against a solvent blank. Infrared spectra of the powdered compound in Nujol mulls or KBr discs were recorded on a Perkin-Elmer 983 spectrophotometer calibrated with polystyrene. Electron spin resonance spectra of the powdered solid and of solutions in dichloromethane were recorded at room temperature and liquid nitrogen temperature on a Varian E3 spectrometer calibrated with diphenylpicrylhydrazyl (g = 2.003).

Magnetic Moment.—The magnetic moment of the solid compound was determined at room temperature (20 °C) on a Faraday balance calibrated with [Ni(H₂NCH₂CH₂NH₂)₃]-S₂O₃. The magnetic moment was calculated assuming the Curie law.

Microanalyses.—Carbon and H analyses were determined by the microanalytical unit at Reading, and P and S by X-ray fluorescence at the Esso Chemical Research Centre, Abingdon.

X-Ray Crystallography.—Suitable crystals of [Fe{S₂P-(OPrⁱ)₂}₃] were obtained by recrystallisation from n-heptane.

Crystal data. C₁₈H₄₂FeO₆P₃S₆, M = 695.5, monoclinic, space group $C2/c$, Z = 4, with cell dimensions a = 11.030(9), b = 27.11(1), c = 11.657(8) Å, β = 87.5(1)°, U = 3 481.9 Å³, D_m = 1.33, D_c = 1.34 g cm⁻³, λ(Mo-K_a) = 0.7107 Å, μ(Mo-K_a) = 9.64 cm⁻¹, F(000) = 1 460.

Precession photographs established the preliminary cell constants and space group. A crystal of dimensions 1.20 × 0.45 × 0.25 was mounted on a Stoe STAD12 diffractometer and data were collected via variable width ω scan. Background counts were 10 s and the scan rate of 0.033° s⁻¹ was applied to ω width of (1.5 + sin μ/tan θ). 3 110 Independent reflections with 2θ < 50° were measured of which 1 773 with I > 3σ(I) were used in subsequent calculations. The Patterson function was used to determine the positions of the iron atom which occupies special positions (4a) on the two-fold axis. The remaining atoms were located from a Fourier map. Hydrogen atoms were placed in tetrahedral positions. Methyl groups were refined as rigid groups. Hydrogen atoms on the same carbon atom were given equivalent thermal parameters. Non-hydrogen atoms were refined anisotropically via full-matrix least squares; the final R was 0.063 (R' 0.065). Scattering factors and dispersion corrections were taken from ref. 3. The final difference-Fourier maps showed no important features and in the final cycles of refinement, no shift was greater than 0.05σ. Calculations were carried out using SHELX 76[4] at the University of Manchester Computer Centre.

Materials.—Iron(III) oxide (of 99 and 99.9% purity) and anhydrous FeCl₃ were purchased from Alfa. Specpure iron powder was from Johnson Matthey. O,O'-Di-isopropyl phosphorodithioic acid was prepared from isopropyl alcohol and P₄S₁₀.[5]
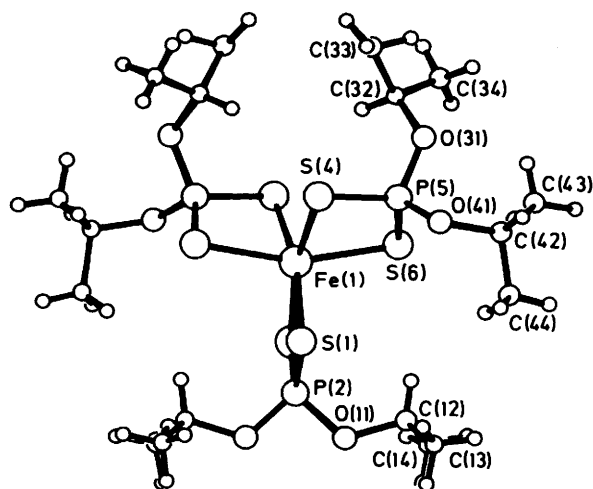
Figure 1. The structure of [Fe{S₂P(OPr^i)₂}₃]

Table 1. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Fe(1)	0	1 452	2 500
S(1)	180(2)	2 144(1)	1 137(2)
P(2)	0	2 589(1)	2 500
S(4)	553(2)	889(1)	871(2)
P(5)	2 197(2)	894(1)	1 499(2)
S(6)	2 142(2)	1 302(1)	2 937(2)
O(11)	1 050(4)	2 979(2)	2 587(4)
C(12)	2 326(6)	2 824(3)	2 656(7)
C(13)	2 753(9)	3 023(5)	3 753(10)
C(14)	2 996(9)	3 025(5)	1 614(10)
O(31)	2 722(5)	363(2)	1 706(5)
C(32)	2 079(11)	5(4)	2 471(11)
C(33)	1 602(17)	−414(5)	1 704(17)
C(34)	2 971(18)	−149(8)	3 318(18)
O(41)	3 126(4)	1 097(2)	556(4)
C(42)	4 412(6)	1 185(3)	804(8)
C(43)	5 154(9)	925(6)	−126(12)
C(44)	4 604(10)	1 728(4)	858(11)

Results and Discussion

Structure of [Fe{S₂P(OPr^i)₂}₃].—The structure and atom numbering are shown in Figure 1. Final co-ordinates are given in Table 1 and bond lengths and angles in Table 2. The structure consists of discrete molecules of [Fe{S₂P(OPr^i)₂}₃] with a distorted octahedral geometry. The molecules have imposed C_2 symmetry; the iron atom and one phosphorus atom, P(2), are on the two-fold axis. The unique Fe–S distances are 2.461(2), 2.492(2), and 2.473(2) Å.

The distortion from octahedral can be expressed in various ways.[6] In [Fe{S₂P(OPr^i)₂}₃] the angle between the sulphurs on opposite sides of the molecule, the *trans* sulphur angle S(1)–Fe–S(4'), is 165.8(1)° compared with 180° for a regular octahedron. The twist angle (θ) between the upper and lower triangles of the co-ordination polyhedron is 20.15° compared with 30.0° for a symmetrical octahedron and 0° for a trigonal prism. Least-squares planes calculations show that the iron atom lies 0.11 Å from the chelate ring S(4),P(5),S(6); but, because of imposed symmetry, it is coplanar with S(1),P(2), S(1'). The structure is discussed further below as part of a general discussion of structure and bonding in the phosphorodithioates and the closely related dithiocarbamates.

Spectra and Magnetic Moment.—Characteristic features of the i.r. spectrum, and the u.v.–visible and e.s.r. spectra are listed in Table 3. The magnetic susceptibility was 2.699×10^{-10} m² g⁻¹ at 293 K corresponding to a magnetic moment of 5.92 B.M. The compound is, therefore, a high-spin complex of iron(III).

The i.r. and u.v.–visible spectra agree with those reported previously, for example, for 'unstable' [Fe{S₂P(OEt)₂}₃] prepared from iron(III) chloride.[2]

Interpretation of the e.s.r. spectra of iron(III) sulphur complexes has aroused controversy. Most work has been done with the dithiocarbamates because they present spin-crossover phenomena.[7] The problems have been attributed to e.s.r.-active impurities in the iron(III) compounds, probably manganese(III)[8] and copper(II).[7] A pure sample of the high-spin complex [Fe{S₂C(pyr)}₃] (pyr = pyrrolidin-1-yl) showed a strong resonance near g 4.3 and weaker resonances near g 7.7, 6.2, and 2, at 85 K.[7] Our spectrum (Table 3) is similar to that of [Fe{S₂C(pyr)}₃]. In particular, a strong g 4—5 signal is characteristic of high-spin octahedral iron(III). The g 4—5 signal is the only signal which can be observed at room temperature. This accords with our experience with phosphorodithioato-complexes provided they are prepared from highly pure iron

Table 2. Molecular dimensions; distances (Å) and angles (°)*

Fe(1)–S(1)	2.461(2)	O(11)–C(12)	1.474(7)
Fe(1)–S(4)	2.492(2)	C(12)–C(13)	1.484(12)
Fe(1)–S(6)	2.473(2)	C(12)–C(14)	1.497(12)
S(1)–P(2)	1.998(2)	O(31)–C(32)	1.478(10)
P(2)–O(11)	1.574(5)	C(32)–C(33)	1.553(19)
S(4)–P(5)	1.985(2)	C(32)–C(34)	1.483(19)
P(5)–S(6)	2.007(3)	O(41)–C(42)	1.478(9)
P(5)–O(31)	1.574(5)	C(42)–C(43)	1.504(12)
P(5)–O(41)	1.570(5)	C(42)–C(44)	1.490(12)

S(1)–Fe(1)–S(4)	88.00(7)	S(6)–P(5)–O(31)	111.96(25)
S(1)–Fe(1)–S(6)	101.94(7)	S(4)–P(5)–O(41)	108.87(21)
S(4)–Fe(1)–S(6)	81.50(7)	S(6)–P(5)–O(41)	112.72(23)
S(1)–Fe(1)–S(1')	80.64(7)	O(31)–P(5)–O(41)	101.23(28)
S(1)–Fe(1)–S(4')	165.80(7)	Fe(1)–S(6)–P(5)	84.97(8)
S(1)–Fe(1)–S(6')	92.47(7)	P(2)–O(11)–C(12)	121.21(43)
S(4)–Fe(1)–S(4')	104.41(8)	O(11)–C(12)–C(13)	106.4(6)
S(4)–Fe(1)–S(6')	86.95(7)	O(11)–C(12)–C(14)	106.9(7)
S(6)–Fe(1)–S(6')	161.12(8)	C(13)–C(12)–C(14)	113.7(8)
Fe(1)–S(1)–P(2)	86.84(9)	P(5)–O(31)–C(32)	121.5(5)
S(1)–P(2)–O(11)	114.12(19)	O(31)–C(32)–C(33)	107.4(10)
S(1)–P(2)–S(1')	105.70(13)	O(31)–C(32)–C(34)	105.7(11)
S(1)–P(2)–O(11')	113.71(19)	C(33)–C(32)–C(34)	115.4(13)
O(11)–P(2)–O(11')	95.69(26)	P(5)–O(41)–C(42)	121.48(49)
Fe(1)–S(4)–P(5)	84.90(9)	O(41)–C(42)–C(43)	106.3(7)
S(4)–P(5)–S(6)	108.54(11)	O(41)–C(42)–C(44)	107.8(7)
S(4)–P(5)–O(31)	113.42(24)	C(43)–C(42)–C(44)	114.7(9)

* Primed atoms refer to the symmetry element $-x, y, \frac{1}{2}-z$.

Table 3. I.r.,[a] u.v.–visible, and e.s.r. details of [Fe{S₂P(OPr^i)₂}₃]

$\tilde{\nu}$/cm⁻¹ [b] 2 950 (CH₃), 1 450w, 1 380m, 1 370m, 1 178m 1 138 (Pr^i), 1 010s (P–O–C), 788m, 650m, 550m (P–S), 540w, 450w (Pr^i), 370vw (Fe–S)

$\lambda_{max.}$/nm (ε/dm³ mol⁻¹ cm⁻¹)[c] 220 (12 700), 250 (sh) (8 320), 360 (6 850), 500 (2 990), 595 (3 020)

$$\text{E.s.r.}^d \begin{cases} \text{solid (293 K): } g = 4.1\text{—}4.6 \\ \text{solid (77 K): } g = 4.2305 \\ \text{in toluene (77 K): } g = 7.575, 5.349, 4.609 \end{cases}$$

[a] For assignments see, for example, I. Haiduc, I. Silaghi-Dumitrescue, R. Grecu, R. Constantinescu, and L. Silaghi-Dumitrescu, *J. Mol. Struct.*, 1984, **114**, 467. [b] Powder in KBr disc; s = strong, m = medium, w = weak, vw = very weak. [c] Compound dissolved in n-heptane. The solutions obeyed Beer's law. [d] For compound prepared from specpure iron (see text).
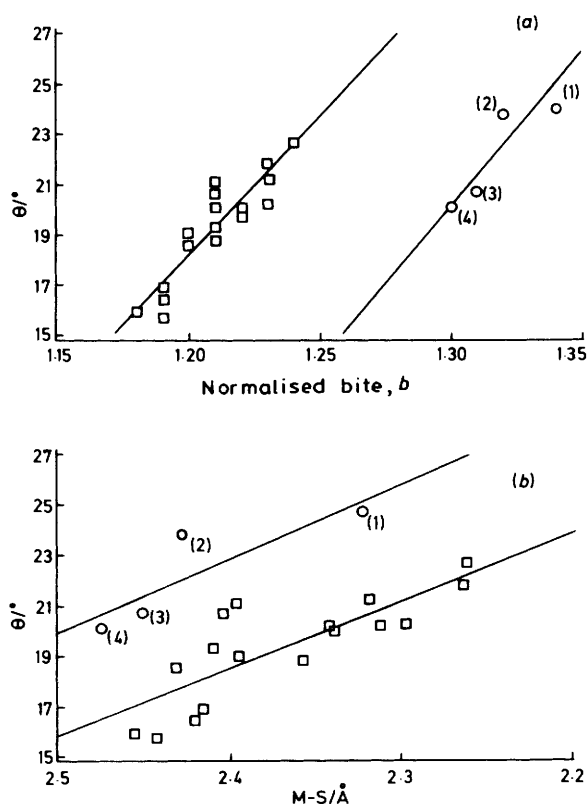
(I)   (II)

Figure 2. (a) Plot of twist angle (θ) versus normalised bite for selected [M{S₂P(OR)₂}₃] structures (○) [M = Co, R = Me (1);[13] M = Cr, R = Et (2);[11] M = V, R = Et (3);[10] M = Fe, R = Prⁱ (this work)(4)] and [M(S₂CNR₂)₃] structures[6c,9] (□). The twist angle θ is 30° for octahedral and 0° for trigonal prismatic structures. The normalised bite is the ratio (L–L)/(M–L) where L–L is the distance between the sulphur atoms in the chelating ligands and M–L is the metal–sulphur distance. Note that distortion from octahedral symmetry decreases as the twist angle increases. Least-squares lines are plotted through each set of data. (b) Plot of twist angle (θ) versus M–S bond length. Structures can be identified as in Figure 2(a)

metal or iron(III) oxide. However, preparations from a less pure iron(III) oxide showed additional resonances in the g 2 region as a solid and in solution at room and liquid nitrogen temperatures. These additional peaks are due to paramagnetic impurities, for example Mnᴵᴵ or Cuᴵᴵ. In fact, we could not observe signals from a manganese(III) phosphorodithioate at room temperature. It is clear then that the e.s.r. spectra of pure Feᴵᴵᴵ phosphorodithioates are similar to pure Feᴵᴵᴵ dithiocarbamates and that problems of extra bands for the phosphorodithioates, as with the dithiocarbamates, are due to impurities, most probably copper.

Preparative Chemistry.—The preparation of a stable sample of an iron(III) phosphorodithioate complex has, in the past, been difficult. The substance prepared by reacting FeCl₃ with diethyl phosphorodithioic acid in methanol is stable only for 'several hours'.[2] We found that compounds prepared from FeCl₃ were unstable, becoming liquid after keeping for a few hours. However, the compounds prepared from iron metal or Fe₂O₃ are stable in air indefinitely. We suspected that the instability was due to the presence of chloride. Hydrolysis on exposure to air generates some hydrochloric acid and leads to acid-catalysed decomposition of the phosphorodithioate complex. We showed by qualitative tests the presence of chloride in the product prepared from FeCl₃. We found also
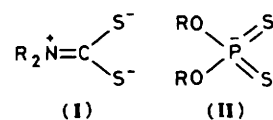
that when we added pyridine or butylamine to the reaction mixture of FeCl₃ and phosphorodithioic acid in methanol the iron(III) phosphorodithioate complexes prepared were stable in air for weeks. This confirms our idea that the decomposition is due to acid (which is rendered ineffective by the amines). Clearly, the preferred starting substance for the preparation of the Feᴵᴵᴵ dialkyl phosphorodithioato-complexes is iron metal or Fe₂O₃.

Structure and Bonding of Phosphorodithioato- and Dithiocarbamato-complexes.—Our determination of the structure of [Fe{S₂P(OPrⁱ)₂}₃] gives us the opportunity of discussing some general features of structure and bonding of phosphorodithioates and the closely related dithiocarbamates (R₂-NCS₂⁻). Iron–sulphur distances in 17 dithiocarbamato-complexes of iron(III) with a FeS₆ core have been listed.[9] We include in our discussion these compounds and other Mᴵᴵᴵ compounds of known structure, viz. [V{S₂P(OEt)₂}₃],[10] [Cr{S₂P(OEt)₂}₃],[11] [Co(S₂CNEt₂)₃],[12] and [Co{S₂-P(OMe)₂}₃].[13] The structure of [Mn(S₂CNEt₃)₃], which is high-spin (t₂g³eg¹) has also been determined[14] but the molecule is very much distorted by the Jahn–Teller effect and so is not included in our general discussion. Features of general interest are distortion from octahedral, metal–sulphur bond lengths, and covalent contributions to the metal–sulphur bond.

Previously distortions from octahedral have been related to the ligand bite angle;[6] Kepert has plotted angle of twist (θ) against normalised bite (b) for 158 complexes of the type [M(bidentate)₃] and shown that the majority of compounds conform to a theoretical straight line obtained from repulsion energy calculations[6c] (θ and b are defined in Figure 2). However, these calculations cannot account for the twist angles in the tris(dithiocarbamate) and tris(phosphorodithioate) complexes. This is shown by Figure 2(a) where the twist angles are plotted against the ligand bite. The linear relationship between twist angle and ligand bite holds for dithiocarbamates and phosphorodithioates, but [M(S₂CNR₂)₃] and [M{S₂-P(OR)₂}₃] fall *not* on the same line but on parallel straight lines with intercepts differing by 0.087 in ligand bite. Similarly, plots of twist angle against M–S bond length are parallel straight lines [Figure 2(b)]. We see, then, that at a particular twist angle M–S bonds are generally shorter, by ca. 0.16 Å [the difference in intercepts in Figure 2(b)] for the S₂CNR₂ complexes than for the S₂P(OR)₂ complexes. This is clearly not a steric effect otherwise the S₂CNR₂ and S₂P(OR)₂ complexes would lie on one line in accordance with Kepert's theory.

We suggest that we are, in fact, seeing the different donor strengths of the ligands, phosphorodithioates being poorer donors than dithiocarbamates. Another way of expressing this is to say that there is less covalency in the M–S bond in phosphorodithioates than in dithiocarbamates. This conclusion is in accordance with deduction from X-ray photoelectron[15] and ultraviolet photoelectron[16] spectroscopic measurements and quantum mechanical calculations.[17] The difference can be rationalised[18] by the contribution of structures (I) and (II). In (I) the electron density on the sulphurs is enhanced; in (II) the electron density is diminished by back-donation from sulphur to the 3d orbitals of the phosphorus. Some evidence is that the P–S distances in phosphorodithioato-complexes (1.982—1.997 Å) are shorter than the sum of the P and S single bond radii (2.14 Å). The dithiocarbamates, therefore, form more covalent, stronger and shorter bonds than the phosphorodithioates.

Acknowledgements

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