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Synthesis and Structural Characterisation of High-Spin *cis*-Bis(acetonitrile) Tetrakis(triphenylphosphine oxide)iron(II) Triiodide–Acetonitrile (1/1)

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The title compound, $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.656(3)$, $b = 15.393(3)$, $c = 21.008(5)$ Å, $\alpha = 78.49(2)$, $\beta = 80.07(2)$, $\gamma = 63.21(1)°$. The compound consists of $[Fe(CH_3CN)_2(OPPh_3)_4]^{2+}$ cations, I_3^- anions and acetonitrile solvate molecules. The iron(II) atom is in a pseudo-octahedral environment built up by the CH_3CN ligands in *cis*-positions with Fe–N distances of 2.157(11) and 2.168(16) Å and by four $OPPh_3$ ligands the Fe–O distances varying from 2.076(11) to 2.168(16) Å. Fitting of the Curie–Weiss law equation to the magnetic susceptibility data yielded Curie and Weiss constant, 2.95 $cm^3\ mol^{-1}$ and -2.5 K, respectively.

The first ferrous complexes of composition $[FeX_2(OPPh_3)_2]$, X = Cl or Br) were prepared by direct reaction between triphenylphosphine oxide ($OPPh_3$) and appropriate anhydrous Fe(II) salts in non-aqueous solutions under nitrogen.[1–3] A similar method has been used for the preparation of the $[FeX_2(PPh_3)_2]$-type complexes (X = Cl, Br or I).[4,9]

On the other hand, it was found[6,7] that the pale violet complex $[Fe(OPPh_3)_4(ClO_4)_2]$ can be prepared by direct reaction between $OPPh_3$ and $Fe(ClO_4)_2$ in non-aqueous solution. This complex was also prepared by the reaction between PPh_3 and $Fe(ClO_4)_3$ under dioxygen.[8] $(Bu_4N)[Fe(OPPh_3)(S_2C_2(CF_3)_2)_2]$ was also prepared similarly by two ways direct and indirect reaction.[9]

We have prepared a series of Fe(III) and Fe(II) complexes of composition $[FeX_3(OPPh_3)_2]$ (X = Cl, Br or NCS) and $[Fe(OPPh_3)_4(Z)_2]$ (Z = ClO_4 or I_3) and studied their physicochemical behaviour as well as catalytic activities.[8,10–14] It was found that, except for $[Fe(OPPh_3)_4(ClO_4)_2]$, all other compounds are the catalysts of oxidation of PPh_3 with O_2 to $OPPH_3$. In this paper we report syntheses and structural characterisation of $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$ which has been prepared by several methods.

Experimental

Syntheses. FeI_2 was synthesized according to the literature.[15] Triphenylphosphine oxide was prepared by the catalytic oxidation of PPh_3 (Jansen Chimica) with O_2 in the presence of Fe(III) triphenylphosphine oxide complexes[10] or the title complex at 333 K and atmospheric pressure. The crude $OPPh_3$ was purified with NaOH and $NaClO_3$ in water–acetone mixture under reflux and recrystallized from acetone–water. The melting point (429 K) agrees with that published for $OPPh_3$.[16] Calc. for $C_{18}H_{15}PO$: C 77.68% and H 5.43%. Found: C 77.84% and H 5.30%.

The complex $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$ was prepared by several methods (Fig. 1). In each method the filtered solution was left in a refrigerator. Recrystallization was done from acetonitrile.

Method 1

8.0 mmol of $OPPh_3$ in 40 ml of acetonitrile (Apolda) was transferred to 1.0 mmol of FeI_2 and 2.0 mmol of I_2 in the reaction vessel, stirred and heated (323 K) under a reflux condenser for two hours. Yield 87%.

Method 2

6.0 mmol of PPh_3 in 25 ml acetonitrile was added to 1.5 mmol FeI_2 and 3.0 mmol I_2 in a thermostatted vessel ($T = 323$ K). Under constant stirring, dioxygen was conducted into the vessel for about 2 h. The completion of oxidation of PPh_3 to $OPPh_3$ was ascertained by comparing the electronic absorption spectrum of the reaction

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solution with the spectrum of pure $OPPh_3$ which exhibits four absorption bands with absorption maxima at 254, 260, 265 and 272 nm. This oxidation also took place under air. Yield 85%. This reaction was also tested in dichloromethane.

Method 3

30 ml acetonitrile and 12.5 mmol of aqueous HI were added into a thermostatted vessel ($T = 323$ K) containing 2.7 mmol powdered iron, 1.3 mmol I_2 and 10 mmol PPh_3. The contents were stirred for 3 h under a dioxygen atmosphere. Yield 85%.

Method 4

The thermostatted vessel contained 30 ml acetonitrile solution of 8.0 mmol PPh_3 and 1.1 mmol of $Fe_2(SO_4)3 \cdot 8.8\ H_2O$, 6.0 mmol of KI and 3.0 mmol of I_2; the mixture was stirred continuously (4 h) in dioxygen atmosphere. The course of this reaction was monitored by UV spectra. Yield 80%.

Method 5

The same product was obtained when $FeSO_4 \cdot 7H_2O$ was used instead of hydrate $Fe_2(SO_4)_3$.

Spectral studies. Routine infrared spectra in Nujol were obtained in the range 4000–200 cm^{-1} on a Specord M 80 spectrophotometer. Full-range spectra (4000–50 cm^{-1}) in Nujol were obtained on a Perkin-Elmer 225 spectrophotometer. Electronic spectra (220–800 nm) in acetonitrile solution were recorded on a Specord M 40 spectrophotometer. The Electronic spectrum in Nujol suspension was obtained in the range 230–800 nm. Reflectance spectra were measured on a Beckman UV 5240 spectrophotometer using magnesium oxide as dilutant and reference.

Magnetic susceptibility measurements. Magnetic susceptibilities were measured in the temperature range 77–296 K by the Gouy method (Cahn RM-2) using solid $Hg[Co(SCN)_4]$ as a calibrant.[17] Diamagnetic corrections were calculated from Pascal's constant,[18] and the effective magnetic moments were calculated using the expression $\mu_{eff} = 2.83\,(X_M^{corr} T)^{1/2}$. A diamagnetic correction of 1703×10^{-6} $cm^3\ mol^{-1}$ was used for the title complex.

Thermogravimetric measurements. These were carried out in air (without DTA) using a Derivatograph OD 102 instrument and a platinum crucible. The sample weight used was 100 mg, and the rate of temperature increase was 1 K min^{-1}.

Measurements of catalytic oxidation. Dioxygen uptake was performed by measuring the volume of O_2 taken up at constant temperatures (313–333 K). The reaction vessel with magnetic stirring and gas burette were separately thermostatted, and this apparatus was equipped with a contact manometer, a solenoid valve, relay and rectifiers as described in Ref. 11.

X-Ray structural analysis. Intensity measurements were made on a Nicolet R3m diffractometer using Mo$K\alpha$ radiation (ω-scan mode and scan range $5.0 < 2\Theta < 50.0°$). Two intensity check reflections showed crystal decay of about 10% at the end of the data collection, although the crystal was sealed in a glass capillary. The data set was scaled, and corrected for Lorentz and polarization factors. An empirical absorption correction was made, the maximum and minimum trasmission factors being 0.592 and 0.501, respectively.

Crystal data. $C_{76}H_{66}FeN_2O_4P_4^{2+} \cdot I_6^{2-} \cdot C_2H_3N$, formula weight 2053.59, $a = 14.656(3)$, $b = 15.393(4)$, $c = 21.008(4)$ Å, $\alpha = 78.49(2)$, $\beta = 80.07(2)$, $\gamma = 63.21(1)°$, $V = 4127(2)$ $Å^3$, $D_c = 1.645$ g cm^{-3}, $Z = 2$, $F(000) = 1988$, μ(Mo$K\alpha$) = 25.2 cm^{-1}, space group triclinic $P\bar{1}$.

Structure analysis and refinement. The crystal structure was determined by direct methods. The disordered CH_3CN solvent molecule was refined isotropically. The phenyl groups of the triphenylphosphine oxide ligands were refined as rigid groups with individual isotropic thermal parameters and the H atoms at calculated position (C–H = 0.96 Å and $U = 0.08$ $Å^2$). The final R-index was 0.067, for 6253 observed reflections and 718 parameters refined. The calculations were performed with SHELXTL-Plus software.[19] The program uses neutral atom scattering factors and takes anomalous dispersion into account. The final atomic coordinates and equivalent isotropic thermal parameters with their e.s.d.s for non-hydrogen atoms are given in Table 1.

Results and discussion

Preparation of the complex. The different ways of the preparation of $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$ are shown in Fig. 1. In the case of indirect reactions taking place in the systems Fe^{Z+}–I_3^-–PPh_3–O_2–CH_3CN ($z = 0$, 2 or 3), PPh_3 is autocatalytically oxidized by dioxygen to $OPPh_3$. Free $OPPh_3$ is found after oxidation, if an excess of PPh_3 is used. Thus iron compounds were used in excess (5–10%) in order to hinder the formation of free $OPPh_3$.

Spectral studies. The IR spectrum of the complex showed that the ν(P–O) band is shifted about 41 cm^{-1} to lower energies compared with the free $OPPh_3$,[20] as the result of $OPPh_3$ coordination. The bands lying in the region of 1436, 1120, 996 and 722 cm^{-1} correspond to the ν(-PPh_3) vibrations. Their locations do not change with the coordination of $OPPh_3$ to iron.[21] Valence vibrations of ν(Fe(II)–O) are in the region 440–305 cm^{-1}. A strong absorption band at $\nu = 137$ cm^{-1} was assigned to antisymmetric vibration $\nu(I_3^-)$.[22]

The absorption spectrum of the complex measured in acetonitrile solution exhibits two broad absorption bands at 292 and 362 nm, respectively. These bands are as-

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients[a] ($\times 10^3$) U(eq) for $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$.

Atom	X	Y	Z	U_{eq}
I(1)	−1454 (1)	−208 (1)	1599 (1)	82 (1)
I(2)	−1533 (2)	11 (2)	205 (1)	151 (1)
I(3)	−1540 (1)	−359 (1)	3009 (1)	121 (1)
I(4)	5039 (1)	6256 (1)	2780 (1)	86 (1)
I(5)	4819 (1)	6227 (1)	4186 (1)	113 (1)
I(6)	5206 (1)	6296 (1)	1357 (1)	127 (1)
Fe(1)	2165 (1)	2771 (1)	2583 (1)	37 (1)
P(1)	2513 (3)	4219 (3)	1134 (2)	44 (2)
P(2)	2708 (3)	3917 (3)	3656 (2)	43 (2)
P(3)	2557 (3)	555 (3)	3541 (2)	58 (2)
P(4)	−589 (2)	4020 (2)	2704 (2)	40 (1)
O(1)	2291 (6)	3834 (6)	1823 (4)	47 (4)
O(2)	2251 (7)	3493 (7)	3290 (4)	54 (5)
O(3)	2115 (7)	1643 (6)	3314 (5)	61 (5)
O(4)	549 (6)	3584 (7)	2652 (5)	59 (4)
N(1)	3810 (9)	1952 (9)	2439 (6)	67 (6)
N(2)	2067 (10)	1986 (9)	1866 (6)	66 (7)
N(3)[b]	5302 (30)	−226 (27)	−911 (18)	129 (12)
N(4)[b]	4643 (61)	208 (56)	−1090 (36)	177 (29)
C(32)[b]	3819 (48)	1520 (48)	−755 (30)	151 (22)
C(41)[b]	4499 (35)	410 (34)	−840 (22)	74 (11)
C(31)[b]	3877 (97)	1132 (93)	−766 (57)	358 (62)
C(42)[b]	4591 (22)	1947 (21)	−1114 (14)	27 (7)
C(11)	4642 (15)	1514 (14)	2362 (9)	93 (11)
C(12)	5814 (13)	912 (19)	2265 (12)	147 (14)
C(21)	2083 (16)	1624 (12)	1449 (9)	92 (11)
C(22)	1982 (26)	1203 (16)	891 (11)	171 (20)
C(112)	4423 (8)	4240 (6)	773 (5)	70 (8)
C(113)	5473	3801	581	81 (10)
C(114)	5955	2816	485	99 (12)
C(115)	5387	2270	580	98 (11)
C(116)	4336	2709	772	75 (9)
C(111)	3854	3694	868	49 (6)
C(122)	1767 (8)	6138 (7)	456 (4)	63 (8)
C(123)	1419	7151	419	76 (9)
C(124)	1386	7554	965	78 (10)
C(125)	1703	6944	1549	93 (12)
C(126)	2052	5931	1586	71 (9)
C(121)	2084	5528	1040	45 (6)
C(132)	2244 (6)	3907 (7)	−81 (4)	52 (7)
C(133)	1716	3728	−494	65 (8)
C(134)	806	3644	−256	66 (8)
C(135)	423	3740	395	72 (9)
C(136)	950	3919	807	54 (7)
C(131)	1861	4003	570	51 (7)
C(212)	2668 (5)	5783 (6)	3500 (4)	49 (6)
C(213)	2163	6807	3411	69 (8)
C(214)	1119	7281	3323	66 (8)
C(215)	579	6731	3324	66 (8)
C(216)	1083	5707	3413	63 (7)
C(211)	2128	5233	3501	44 (6)
C(222)	2671 (7)	4023 (6)	4975 (4)	54 (7)
C(223)	2421	3804	5640	55 (7)
C(224)	1959	3165	5853	78 (9)
C(225)	1746	2746	5401	76 (10)
C(226)	1995	2965	4735	65 (8)
C(221)	2457	3604	4523	42 (6)
C(232)	4396 (8)	3737 (8)	2807 (5)	84 (10)
C(233)	5445	3390	2612	114 (14)
C(234)	6158	2826	3065	114 (14)
C(235)	5822	2609	3713	101 (12)
C(236)	4773	2957	3909	81 (10)
C(231)	4060	3520	3456	53 (7)
C(312)	1083 (9)	1061 (6)	4571 (6)	80 (10)
C(313)	589	879	5177	106 (14)
C(314)	881	−83	5491	103 (14)
C(135)	1666	−862	5199	111 (13)
C(316)	2160	−680	4593	85 (10)
C(311)	1869	281	4279	66 (8)
C(322)	4172 (9)	697 (6)	3900 (6)	83 (10)
C(323)	5158	346	4091	109 (13)
C(324)	5811	−656	4135	140 (16)
C(325)	5479	−1306	3990	155 (16)
C(326)	4493	−955	3800	99 (10)
C(321)	3840	47	3755	70 (8)
C(332)	3352 (8)	−551 (9)	2512 (6)	84 (10)
C(333)	3274	−1001	2023	106 (13)
C(334)	2350	−1028	1976	134 (20)
C(335)	1503	−606	2420	125 (18)
C(336)	1581	−156	2909	85 (10)
C(331)	2505	−129	2956	67 (8)
C(412)	−580 (7)	3688 (7)	4034 (6)	73 (9)
C(413)	−993	3560	4676	87 (11)
C(414)	−1954	3548	4802	100 (12)
C(415)	−2502	3664	4286	82 (10)
C(416)	−2088	3792	3644	62 (8)
C(411)	−1127	3804	3518	49 (6)
C(422)	−467 (5)	5755 (7)	2172 (4)	59 (8)
C(423)	−847	6772	2002	72 (9)
C(424)	−1890	7370	2133	73 (9)
C(425)	−2552	6951	2433	69 (8)
C(426)	−2172	5934	2602	48 (7)
C(421)	−1129	5336	2472	43 (6)
C(432)	−1867 (7)	4067 (5)	1813 (5)	60 (7)
C(433)	−2191	3600	1457	74 (10)
C(434)	−1702	2579	1488	89 (11)
C(435)	−889	2026	1874	95 (11)
C(436)	−565	2493	2230	80 (9)
C(431)	−1054	3514	2200	47 (6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Population parameters for disordered atoms of the solvent CH_3CN molecule: N(3) 0.60, N(4) 0.40, C(31) 0.55, C(32) 0.50, C(41) 0.50, C(42) 0.35.

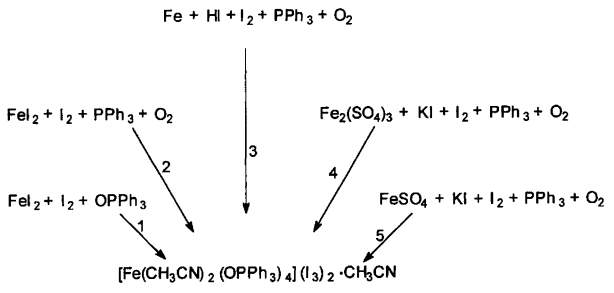

Fig. 1. Preparations of $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$.

signed to I_3^- in fair conformity with results reported[23] for the triiodide anion in ethyl chloride, ethanol or water. Moreover, the spectrum shows four characteristic bands that belong to $OPPh_3$ ($\lambda_{max} = 254$, 260, 265 and 272 nm). These bands are typical of the UV spectra of the aromatic phosphine oxides. Likewise, the spectrum of the complex in Nujol suspension shows the very broad band of I_3^- at 375 nm.

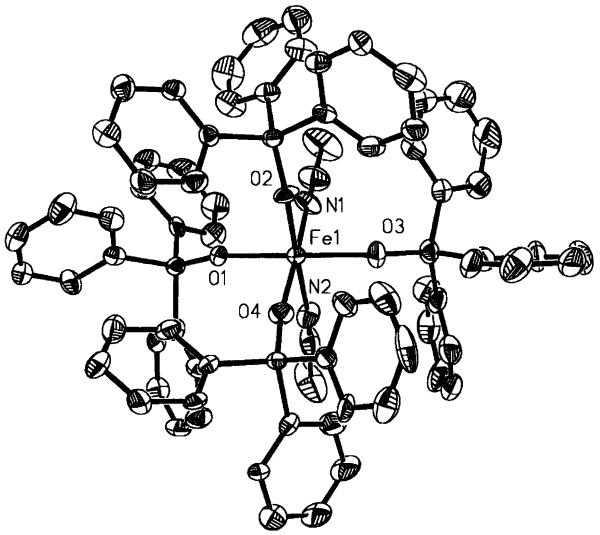

Fig. 2. Structure of $[Fe(CH_3CH)_2(OPPh_3)_4]^{2+}$ cation. Displacement ellipsoids are drawn at the 30% probability level.

The reflectance spectrum shows a strong band at about 360 nm and other weak bands at 1120 and 1390 nm. The former band can be assigned as a charge-transfer band, and the other bands as a d–d transitions.

Magnetic studies. The dependence of magnetic susceptibility and its reciprocal value, as well as magnetic moments, on the temperature range 77–296 K are shown in Fig. 2. Magnetic susceptibility data obey the Curie–Weiss law:

$$X_M^{corr} = C/(T - \Theta)$$

where C and Θ are the Curie and Weiss constants, respectively. The value of the magnetic moment is slightly dependent on temperature ($\mu_{eff} = 4.78$ BM at 77 K and 4.86 BM at 296 K), which indicates a quartet ground state. Calculated values of the constants C and Θ are 2.95 $cm^3\ mol^{-1}$ K and -2.5 K, respectively. A small negative Weiss constant indicates a weak anti-ferromagnetic interaction in the high-spin complex.

Thermal studies. The thermogravimetric data permit the following conclusions. The complex is thermally stable up to 150 °C. At about 170 °C it melts with a decomposition. The rapid exothermic decomposition occurs from 200 to 420 °C. Then the decrease of mass slows down under an exothermic effect. Above 900 °C there remains a 3% residue.

Crystal and molecular structure. A view of the complex cation is shown in Fig. 3. Selected bond lengths and bond angles are given in Tables 2 and 3.

The octahedral complex cation possesses nearly C_2 symmetry, the pseudo-twofold rotation axis bisecting the N(1)–Fe(1)–N(2) angle and passing through Fe(1) (Fig. 3). The CH_3CN ligands are in the *cis*-position, the Fe–N distances are 2.157(11) and 2.168(16) Å and the Fe–O distances are 2.076(11)–2.116(8) Å (Table 2). These distances are compared with those found in another Fe(II) compounds (Table 4). As can be seen, the Fe–N distances found in the high-spin compounds $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$ and

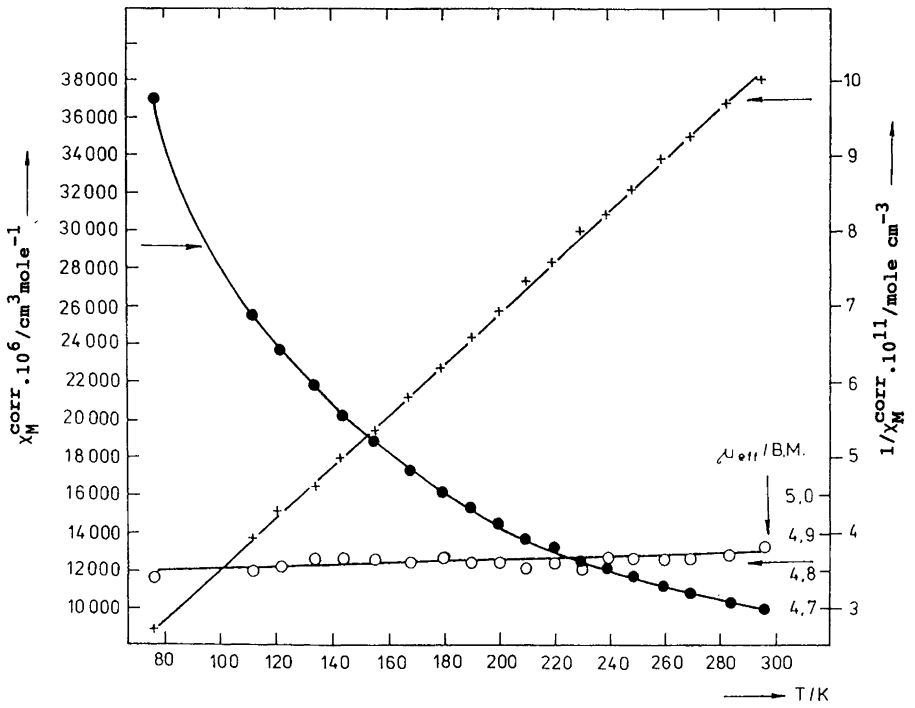

Fig. 3. Magnetic susceptibility and effective magnetic moment as functions of temperature.

Table 2. Selected bond lengths for $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$.

I(1)–I(2)	2.897 (2)	I(1)–I(3)	2.910 (2)
I(4)–I(5)	2.909 (2)	I(4)–I(6)	2.948 (2)
Fe(1)–O(1)	2.096 (8)	Fe(1)–O(2)	2.076 (11)
Fe(1)–O(3)	2.095 (9)	Fe(1)–O(4)	2.116 (8)
Fe(1)–N(1)	2.157 (11)	Fe(1)–N(2)	2.168 (16)
P(1)–O(1)	1.490 (9)	P(1)–C(111)	1.788 (10)
P(1)–C(121)	1.799 (11)	P(1)–C(131)	1.807 (12)
P(2)–O(2)	1.495 (13)	P(2)–C(211)	1.792 (9)
P(2)–C(221)	1.805 (9)	P(2)–C(231)	1.790 (12)
P(3)–O(3)	1.504 (9)	P(3)–C(311)	1.784 (12)
P(3)–C(321)	1.782 (13)	P(3)–C(331)	1.803 (16)
P(4)–O(4)	1.483 (9)	P(4)–C(411)	1.788 (11)
P(4)–C(421)	1.807 (9)	P(4)–C(431)	1.804 (12)
N(1)–C(11)	1.10 (2)	N(2)–C(21)	1.12 (3)
C(11)–C(12)	1.54 (2)	C(21)–C(22)	1.51 (4)

$[Fe^{II}(CH_3CN)_6][Fe^{III}Cl_4]_2$[24] are somewhat longer than those found in low-spin Fe(II) complexes.[24–27] This implies an increased diameter of high-spin Fe(II) as compared to low-spin Fe(II). The average Fe–O distance of 2.096(9) Å is somewhat longer than the corresponding value found in high-spin $[Fe^{III}Cl_2(OPPh_3)_4][Fe^{III}Cl_4]$[13] and $[Fe^{III}Br_2(OPPh_3)_4][Fe^{III}Br_4]$,[14] which are 2.012(5) and 2.00(1) Å, respectively. Again, this implies an increase in diameter of high-spin Fe(II) (0.78 Å) as compared to high-spin Fe(III) (0.645 Å).[28]

The shortest intermolecular interaction is between the triiodide ion and the disordered acetonitrile solvent molecule: C(42)–I(6) $(1-x,\ 1-y,\ -z) = 2.79$ Å. This interaction is much shorter than the sum of the van der Waals radii of the I and C atoms. They may be indicative of larger disorder than that due to only the CH_3CN solvent molecule, some holes between complex cations may be occupied by I^- and I_2 molecules instead of I_3^- and CH_3CN. The other intermolecular distances are 'normal' van der Waals interactions. The data for I–I distances and I–I–I angles of I_3^- anions found in different compounds are summarized in Table 5, and agree well with each other.[29–34] The bond lengths and angles of the ligand molecules are similar to those found previously (Tables 2 and 3.

Catalytic studies. The oxidation of PPh_3 by O_2 in the presence of the title compound is faster than in the presence of $[FeX_3(OPPh_3)_2]$ (X = Cl, Br or NCS) complexes (Table 6).[8,12] With one mole of $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$ used as catalyst, about 250 mol of PPh_3 can be oxidized in the homogeneous phase, whereas with one mole of $[Fe(NCS)_3(OPPh_3)_2]$ a maximum of 100 mol PPh_3 can be oxidized.[10]

Rapid reduction of I_3^- to I^- (the solution becomes decolourized) occurs after adding PPh_3 into our acetonitrile solution of the title compound. The I_3^- anion appears in the catalytic system only at the end of the PPh_3 oxidation. During the catalytic cycle the oxidation state of Fe(II) stays unchanged, as was quoted by the reaction with 2,2′-dipyridyl,[35] since in the presence of a Fe(III) complex of $[FeX_3(OPPh_3)_2]$; X = Cl, Br or NCS the addition of PPh_3 causes a reduction of Fe(III) to Fe(II).[12,36] Then during the oxidation of PPh_3 catalyzed by $[FeX_3(OPPh_3)_2]$ and the title complex the reversible redox reaction $Fe(II) \rightleftharpoons Fe(III)$[12,36] and $I_3^- \rightleftharpoons 3I^-$, respectively, takes place. The reversible redox reaction occurs not only in our investigated catalytic systems but also in others.[37,38]

The highest oxidation activity of the iron(II)–triiodide complex (Table 6) probably depends on at least two factors, the first the slight light oxidizability of I_3^- anions and the second the easy substitution of acetonitrile

Table 3. Selected bond angles for $[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$.

I(2)–I(1)–I(3)	175.7 (1)	I(5)–I(4)–I(6)	178.5 (1)
O(1)–Fe(1)–O(2)	92.7 (4)	O(1)–Fe(1)–O(3)	176.5 (3)
O(2)–Fe(1)–O(3)	89.4 (4)	O(1)–Fe(1)–O(4)	89.5 (3)
O(2)–Fe(1)–O(4)	90.1 (4)	O(3)–Fe(1)–O(4)	93.3(4)
O(1)–Fe(1)–N(1)	87.9 (4)	O(2)–Fe(1)–N(1)	93.1 (5)
O(3)–Fe(1)–N(1)	89.2 (4)	O(4)–Fe(1)–N(1)	175.9 (4)
O(1)–Fe(1)–N(2)	89.0 (4)	O(2)–Fe(1)–N(2)	178.3 (5)
O(3)–Fe(1)–N(2)	89.0 (5)	O(4)–Fe(1)–N(2)	89.8 (5)
N(1)–Fe(1)–N(2)	87.1 (5)	O(1)–P(1)–C(111)	112.5 (5)
O(1)–P(1)–C(121)	110.6 (5)	C(111)–P(1)–C(121)	107.0 (5)
O(1)–P(1)–C(131)	112.5 (6)	C(111)–P(1)–C(131)	107.6 (5)
C(121)–P(1)–C(131)	106.3 (5)	O(2)–P(2)–C(211)	111.5 (5)
O(2)–P(2)–C(221)	109.7 (6)	C(211)–P(2)–C(221)	105.9 (4)
O(2)–P(2)–C(231)	113.6 (6)	C(211)–P(2)–C(231)	106.7 (5)
C(221)–P(2)–C(231)	109.2 (4)	O(3)–P(3)–C(311)	111.1 (5)
O(3)–P(3)–C(321)	113.7 (6)	C(311)–P(3)–C(321)	103.3 (6)
O(3)–P(3)–C(331)	112.6 (6)	C(311)–P(3)–C(331)	106.6 (6)
C(321)–P(3)–C(331)	108.9 (5)	O(4)–P(4)–C(411)	112.3 (5)
O(4)–P(4)–C(421)	111.2 (5)	C(411)–P(4)–C(421)	106.7 (4)
O(4)–P(4)–C(431)	112.2 (5)	C(411)–P(4)–C(431)	106.0 (6)
C(421)–P(4)–C(431)	108.2 (4)	Fe(1)–O(1)–P(1)	155.2 (6)
Fe(1)–O(2)–P(2)	157.9 (6)	Fe(1)–O(3)–P(3)	146.6 (6)
Fe(1)–O(4)–P(4)	172.0 (7)	Fe(1)–N(1)–C(11)	177.9 (19)
Fe(1)–N(2)–C(21)	172.2 (16)		

Table 4. Selected structural parameters of iron(II)acetonitrile complexes.

Complex cation[a]	Low/high-spin	Chromo-phore	Fe–N/Å	Fe–N–C/° N–C/Å	Ref.
$[Fe(CH_3CN)_6]^{2+}$	High	FeN_6	2.190 (0)	175.7 1.09 (1)	24
$[Fe(CH_3CN)_2(dmpe)_2]^{2+}$	Low	FeN_2P_4	1.905 (7)	178.1 (5) 1.129 (7)	25
$[Fe(CH_3CN)_2(Ph_2PCHCHPPh_2)_2]^{2+}$	Low	FeN_2P_4	1.916 (10)	170.6 (11) 1.13 (2)	26
$[Fe(CH_3CN)_2(opdp)_2]^{2+}$	Low	FeN_2P_4	1.894 (4)	– –	27
$[Fe(CH_3CN)_2(OPPh_3)_4]^{2+}$	High	FeN_2O_4	2.157 (11)	177.9 (19) 1.10 (2)	This work
			2.168 (16)	172.2 (16) 1.12 (3)	

[a] dmpe = 1,2-bis(dimethylphosphino)ethane. $Ph_2PCHCHPPh_2$ = *cis*-1,2-bis(diphenylphosphino)ethene. opdp = *o*-phenylenebis-(diphenylphosphine).

Table 5. Selected structural parameters of triiodide anions.

Compound	I(1)–I(2)/Å	I(2)–I(3)/Å	Σ/Å[a]	Ref.
NH_4I_3	3.10	2.82	5.92	29
$[C^+I_3^-][BI_2]$[b]	2.870	2.996	5.87	30
CsI_3	3.030 (15)	2.830 (15)	5.86	29
(MDTTTF)I_3[c]	2.939 (1)	2.924 (1)	5.86	31
$(Bu_4N)I_3$[d]	2.941	2.910	5.85	32
(EDTTTF)I_3[e]	2.927 (1)	2.901 (1)	5.83	31
$[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$	2.897 (2)	2.910 (2)	5.81	This work
	2.909 (2)	2.948 (2)	5.86	
$UO_2(tdpo)_4(I_3)_2$[f]	2.904 (2)	2.909 (2)	5.81	33
$As(C_6H_5)_4I_3$	2.90 (2)	2.90 (2)	5.80	29
$C_8H_4S_8I_3$[g]	2.926 (1)	2.867 (1)	5.79	34

[a] Sum of the I–I distances in I_3^-. [b] 1-(1-Imidazolin-2-yl)-2-thioxoimidazolidinium triiodide-(ethylenethiourea-diiodine). [c] 2-(2-Dithiolylidene)dithiolo[4,5-d]dithiolium triiodide. [d] Tetrabutylammonium. [e] 2-(2-Dithiolylidene)5,6-dihydrothiolo[4,5-b]dithiinium triiodide. [f] Tris(dimethylamido)phosphine oxide. [g] 3,4,3′,4′-Bis(methylenedithio)tetrathiofulvalenium triiodide.

Table 6. Initial rates (v) of PPh_3 oxidation by O_2 for various irontriphenylphosphine oxide catalysts at 323 K.[8,12]

Catalyst	$10^6 \times v$ mol dm^{-3} s^{-1}	r
$FeCl_3(OPPh_3)_2$	1.6	0.984
$Fe(NCS)_3(OPPh_3)_2$	16.7	0.992
$FeBr_3(OPPh_3)_2$	23.0	0.998
$[Fe(CH_3CN)_2(OPPh_3)_4](I_3)_2 \cdot CH_3CN$	291.0	0.985

$c(Fe) = 0.05$ M, $c(PPh_3) = 0.20$ M. r = correlation coefficient.

ligands in the coordination sphere of iron (II) with PPh_3 ligands, which are then oxidized to $OPPh_3$.

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