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OXYGEN TRANSFER FROM IRON NITRATES IN THE PRESENCE OF 2-(DIPHENYLPHOSPHINE OXIDE)PYRIDINE ($OPPh_2py$). MOLECULAR STRUCTURE OF $Fe(NO_3)_2Cl(OPPh_2py)\cdot CH_2Cl_2$

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Abstract—$[Fe(Cl)_4][Fe(NO_3)_2(OPPh_2py)_2]$, **2**, and $[Fe(NO_3)_2(Cl)(OPPh_2py)]$, **3**, were obtained when $[Fe(Cl)_4][Fe(Cl)_2(OPPh_2py)_2]$, **1**, was allowed to react with respectively 2 and 4 eq. silver nitrate. Complexes **2** and **3** catalysed the autoxidation of cyclohexene. They transfer the oxygens of their nitrato groups to phosphines. Complex **3** has been characterized by single crystal X-ray diffraction. The bite of the $OPPh_2py$ ligand repels the presence of the chlorine atom in the $Fe(NO_3)_2$ plane of **3** which influences the geometric features of the nitrato groups, their oxygen transfer ability.

The selective oxidation of organic compounds has gained much attention in the chemical industry in recent years. An important class of such reactions is the oxygen atom transfer from metal complexes which offer non-radical pathways for such selective oxidations.[1] We have shown that oxidation of organic substrates can be mediated by iron nitrates.[2–5] These reactions proceed by the insertion of oxygen atoms of the coordinated nitrates into the substrate, with the formation of the oxidized product. The resulting iron–nitrosyl complex then recombines with dioxygen. Such Fe—NO/Fe—NO_3 systems are potential catalysts for the direct epoxidation of olefins by molecular oxygen. In our search for the best ligand environment for such systems, we became interested in bidentate ligands with two different coordination sites and first considered the 2-(diphenylphosphine oxide) pyridine ligand, $OPPh_2py$, which appeared as a promising candidate for our systems.[6] In this paper, we report the synthesis, structure and reactivity of iron nitrates in the presence of $OPPh_2py$ and show that these are capable of transferring molecular oxygen.

EXPERIMENTAL

General procedures

All experiments were carried out under nitrogen, argon or oxygen using Schlenk tube techniques. Reagent grade solvents were purified by published procedures and stored under nitrogen. Silver nitrate and triphenylphosphine were purchased from Aldrich and used without further purification. Trimethylamine oxide (Aldrich) was sublimed prior use. The ligand 2-(diphenylphosphino)pyridine was prepared according to the literature;[7] its reaction with trimethyl amine oxide following a published procedure[8] afforded quantitative yields of 2-(diphenylphosphine oxide)pyridine.

Elemental analyses were performed by the Service Central de Microanalyses of the CNRS. Infrared spectra were recorded as Nujol mulls or KBr pellets on a Bruker FT-IFS 45 spectrometer. ESR spectra were measured on a Bruker 200 SRC spectrometer equipped with a variable-temperature accessory, both in the solid state and in solution. ^{31}P NMR spectra were recorded on a Bruker WH 90 spectrometer. ^{31}P chemical shifts are given in parts per million downfield from external H_3PO_4. GC/MS coupling experiments were performed on

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a Finnigan MAT INCOS 500E spectrometer associated with a Varian-3400 chromatograph equipped with a DB-5 25 m × 0.32 mm capillary column.

Synthesis of $[Fe(Cl)_4][Fe(Cl)_2(OPN)_2]$, **1**

A solution of 1.33 g (4.75 mmol) of 2-(diphenylphosphine oxide)pyridine, OPN, in dichloromethane (50 cm^3) is added to a solution of anhydrous iron(III) chloride (0.77 g, 4.75 mmol) in 50 cm^3 of CH_2Cl_2/CH_3CN 10/1. The reaction mixture was stirred at RT for 24 h and filtered. The filtrate was evaporated to dryness and the residue washed with pentane, and dried *in vacuo* (1.87 g, 89%). Found: Fe, 13.1; P, 6.2. Calc. for $Fe_2Cl_6C_{34}H_{28}N_2P_2O_2Cl_2$: Fe, 12.6; P, 7.0%. IR (KBr pellets, cm^{-1}): ν(C=N), 1589; ν(P=O), 1167; ν(OP—C), 1124; ν(Fe—Cl), 380 and 332. Λ_M (10^{-3} M solution in CH_2Cl_2): 158 cm^2 ohm^{-1} mol^{-1}.

Synthesis of $[Fe(Cl)_4][Fe(NO_3)_2(OPN)_2]$, **2**

A solution of silver nitrate (0.105 g, 0.618 mmol) in acetonitrile (20 cm^3) was added dropwise to a solution of **1** (0.274 g, 0.309 mmol) in CH_2Cl_2 (50 cm^3) at RT. Instantaneous formation of a white precipitate of AgCl resulted; the suspension was stirred for 2 h before filtration. The solution was evaporated to dryness. The residue was washed with pentane and dried *in vacuo* to yield 0.233 g of **2** (80%). Found: Fe, 11.4; N, 5.6; Cl, 14.9; P, 6.1; C, 44.1; H, 3.2. Calc. for $Fe_2Cl_4C_{34}H_{28}N_4P_2O_8$: Fe, 11.9; N, 6.0; Cl, 15.1; P, 6.6; C, 43.6; H, 3.0%. IR (KBr pellets, cm^{-1}): ν(C=N), 1589; ν(P=O), 1167; ν(OP—C), 1125; $\nu(NO_3)$, 1533, 1384, 1272; ν(Fe—Cl), 382. Λ_M (10^{-3} M solution in CH_2Cl_2): 126 cm^2 ohm^{-1} mol^{-1}.

Synthesis of $[Fe(NO_3)_2(Cl)(OPN)]$, **3**

The same experimental procedure that afforded **2** was applied to 0.770 g (4.53 mmol) of $AgNO_3$, 1.00 g of complex **1** (1.13 mmol) to prepare **3**. Yield: 0.986 g, 88%. Found: Fe, 10.8; N, 8.1; Cl, 7.2; P, 6.4. Calc. for $FeC_{17}H_{14}N_3ClO_7P$: Fe, 11.3; N, 8.2; Cl, 7.2; P, 6.3%. IR (KBr pellets, cm^{-1}): ν(C=N), 1591; ν(P=O), 1166; ν(OP—C), 1123; $\nu(NO_3)$, 1532, 1384, 1270; ν(Fe—Cl), 338. Λ_M (10^{-3} M solution in CH_2Cl_2): 41 cm^2 ohm^{-1} mol^{-1}. Slow diffusion of pentane into a CH_2Cl_2 solution of **3** afforded crystallographic quality crystals of its CH_2Cl_2 solvate $[Fe(NO_3)_2(Cl)(OPN)\cdot CH_2Cl_2]$, **3s**.

General procedure for the oxidation tests

The iron complexes (*ca* 0.1 mmol) were dissolved in 5 cm^3 of CH_2Cl_2 or CH_3CN, and cyclohexene (10 mmol) was added to the solution together with n-octane as an internal standard for GC analyses. The resulting solution was stirred under an atmosphere of oxygen at room temperature and the oxidation products monitored by GC analysis of aliquot samples. The oxygenated products were identified by GC-MS coupling by comparison with authentic samples.

Molecular structure of $[Fe(NO_3)_2(Cl)(OPN)\cdot CH_2Cl_2]$, **3s**

Crystallographic quality crystals of $FeC_{18}H_{16}N_3Cl_3O_7P$, **3s**, (M = 579.52), were isolated as yellow parallelepipeds. They were grown by allowing a layer of pentane to diffuse slowly into a solution of **3** in dichloromethane at RT; they were washed with pentane, then dried under a stream of argon.

A summary of crystal data and intensity collections for **3s** is given in Table 1. The unit cell constants were refined by least squares from angle data for 25 reflections. Based on systematic absences, the space group for **3s** was determined to be $P2_{1/n}$.

Table 1. Crystal and data collection parameters for complex **3**

Empirical formula	$FePCl_3O_7N_3C_{18}H_{16}$
Formula weight	579.52
Crystal shape	parallelepipedic
Crystal dimensions (mm)	0.3, 0.15, 0.10
Crystal system	monoclinic
Space group	$P2_{1/n}$
Z value	4
No. reflns used for unit cell	25
Lattice parameters	
a (Å)	9.138(6)
b (Å)	15.69(1)
c (Å)	16.68(1)
β (°)	94.50(5)
$D_{calc.}$ (g cm^{-3})	1.614
μ (cm^{-1})	8.47
$F(000)$	1172
T (°C)	25
Reflns measured	4290
Reflns unique	2981
Reflns obsd	2067
No. variables	213
R	0.071
R_w	0.074

Diffraction data were collected on an Enraf–Nonius CAD 4 automated diffractometer at room temperature. Intensities were corrected for Lorentz and polarization factors but not for absorption. All computations were performed on a PDP 11/44 computer using the Enraf–Nonius crystallographic software package. The structure was solved by direct methods and refined by a combination of Patterson, difference-Fourier and full-matrix least squares refinement techniques using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed in calculated positions with isotropic temperature factors fixed at 5 Å^2 and were not refined; these values were included in the final full-matrix refinement for all non-hydrogen atoms. The function minimized was $\Sigma w(F_o - F_c)^2$, where $w = V_o/\sigma^2$. Final R and R_w values were respectively 0.071 and 0.074. The atomic scattering factors were taken from the *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, U.K., 1968.

Principal bond distances and angles are given in Table 2.

RESULTS

Prior to the present study, 2-(diphenylphosphine oxide)pyridine, $OPPh_2py$, had been obtained by oxidation of the parent phosphine with hydrogen peroxide[9] and a very limited amount of coordination chemistry has been accomplished. To the best of our knowledge, the only X-ray structure reported to date concerns $CoCl_2(OPPh_2py)_2$ where the two $OPPh_2py$ ligands are coordinated to the metal by both their oxygen and nitrogen atoms.[10]

Nitrato iron complexes

Allowing 2-(diphenylphosphine oxide)pyridine, OPN, and anhydrous $FeCl_3$ to react yielded the ionic complex **1**, which analyses as $[FeCl_4][FeCl_2(OPN)_2]$. Bidentate coordination of the OPN ligand by the oxygen of the phosphoryl and the nitrogen of the pyridine moiety is ascertained by the presence, in the IR spectrum for **1** of shifted ν(P=O) and pyridine ν(C=N) vibrations respectively at 1167 and 1589 cm^{-1} (1202 and 1572 cm^{-1} in the free ligand). The IR spectra showed two bands in the region attributable to Fe—Cl vibrations: a broad and intense vibration at 384 cm^{-1} was taken to indicate the presence of the $[FeCl_4]^-$ anion in complex **1** while the weak vibration at 332 cm^{-1} was assigned to the Fe—Cl moiety in the cation. The ionic nature of **1** was further confirmed by conductivity measurements in CH_3CN where it was found to behave as a 1 : 1 electrolyte.

The reaction of **1** with 2 eq. $AgNO_3$ afforded compound **2**. The IR spectrum for **2** showed the disappearance of the ν(Fe—Cl) at 332 cm^{-1} while new absorptions were measured at 1533 and 1272 cm^{-1} in the regions generally assigned to bound nitrates;[11] a vibration detected only for the KBr pellets at 1385 cm^{-1} is attributed to the NO_3-anion due to Br^- exchange.[12] IR spectra also indicated coordinated ν(P=O) and ν(C=N) at, respectively, 1167 and 1589 cm^{-1} and one broad and an intense ν(Fe—Cl) at 382 cm^{-1}, consistent with the $[FeCl_4]^-$ anion. Conductivity measurements showed **2** to be ionic. The spectral and analytical data for **2** indicate the formation of $[FeCl_4][Fe(NO_3)_2(OPN)_2]$.

When the reaction of **1** was conducted with 4 eq. $AgNO_3$, the molecular complex **3** was isolated and analysed as $Fe(NO_3)_2Cl(OPN)$. In its infrared spectra, the $\nu(NO_3)$ stretching frequencies are measured at 1532 and 1270 cm^{-1}; the presence of coordinated OPN was evidenced by the ν(P=O) at 1167 cm^{-1} and ν(C=N) at 1589 cm^{-1}. The ν(Fe—Cl) vibration band was detected at 338 cm^{-1}. The structure of compound **3** was unambiguously established by a single-crystal X-ray study of its CH_2Cl_2 solvate $Fe(NO_3)_2Cl(OPN) \cdot CH_2Cl_2$, **3s** (*vide infra*).

Table 2. Selected bond distances (Å) and bond angles (°) for complex **3s** with esds in parentheses

Fe—Cl	2.250(3)	P—O(1)	1.498(7)
Fe—O(1)	2.011(6)	N(1)—O(2)	1.27(1)
Fe—O(2)	2.155(8)	N(1)—O(3)	1.28(1)
Fe—O(3)	2.099(8)	N(2)—O(5)	1.25(1)
Fe—O(5)	2.136(8)	N(2)—O(6)	1.27(1)
Fe—O(6)	2.174(8)	N(1)—O(4)	1.21(1)
Fe—N(3)	2.178(8)	N(2)—O(7)	1.21(1)
O(1)—Fe—Cl	176.0(2)	O(1)—Fe—N(3)	80.6(3)
O(2)—Fe—O(3)	60.4(3)	O(2)—N(1)—O(3)	114.5(8)
O(5)—Fe—O(6)	59.3(3)	O(5)—N(2)—O(6)	115.2(9)

X-Ray crystal structure of $Fe(NO_3)_2$ $Cl(OPN) \cdot CH_2Cl_2$, **3s**

The structure of compound **3s**, which was found to crystallize as the $Fe(NO_3)_2Cl(OPN) \cdot CH_2Cl_2$ solvate, is illustrated in Fig. 1 with atomic labelling used. Selected bond lengths and angles are given in Table 2.

The geometry of the complex is that of a distorted pentagonal bipyramid with the oxygen of the OPN ligand and the chlorine atom at the apices

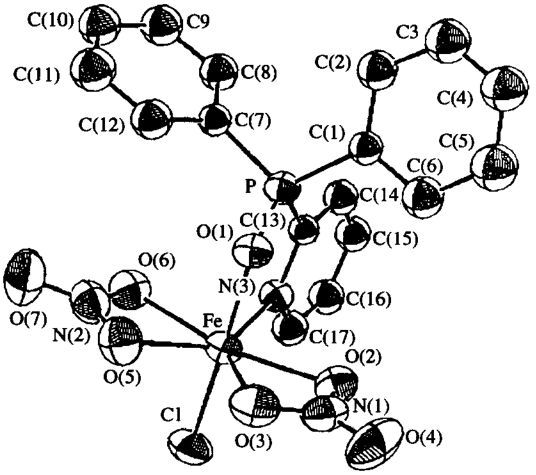

Fig. 1. Molecular structure of $Fe(NO_3)_2Cl(OPPh_2py)$ 3.

[O(1)—Fe—Cl = 176.0(2)°] and the nitrogen of the OPN ligand and two oxygen atoms of each of the two nitrate ligands forming an approximate planar pentagonal arrangement around iron.

The iron–nitrate structural parameters are very similar to those found for other symmetrical bidentate nitrato complexes.[3,13] The difference between the distances of the iron atom and the two coordinated oxygen atoms of the nitrato groups, Fe—O(2) and Fe—O(3) on the one hand, Fe—O(5) and Fe—O(6) on the other hand, are respectively 0.056 and 0.036 Å, i.e. of the order of magnitude where the coordinated nitrate ligand is considered to be symmetrically bidentate.[13] The geometry of the nitrate ligands is conventional: the O(2)—N(1)—O(3) and O(5)—N(2)—O(6) angles involving the coordinated oxygens are less than 120° [114.5(8) and 115.2(9)°]; the terminal N(1)—O(4) and N(2)—O(7) bonds [1.21(1) Å] are slightly shorter than the N—O bonds involving coordinated oxygens [N(1)—O(2): 1.27(1) Å and N(1)—O(3): 1.28(1) Å; N(2)—O(5): 1.25(1) Å and N(2)—O(6): 1.27(1) Å].

The Fe—Cl distance [2.250(3) Å] is comparable to that found for $Fe(NO_3)_2Cl(OPPh_3)_2$[2] [2.257(1) Å] or $Fe(NO_3)Cl_2(HMPA)_2$ [2.257(1) and 2.273(1) Å][3] within experimental uncertainties.

The Fe—O(1) (phosphoryl) bond distance of 2.011(6) Å is significantly longer than the Fe—O(P) distances in $Fe(NO_3)_2Cl(OPPh_3)_2$[2] [1.970(2) and 1.950 Å] or $Fe(NO_3)Cl_2(HMPA)_2$[3] [1.966(2) and 1.963(2) Å]. In the latter two complexes, the phosphoryl oxygens are *trans* to each other, while in complex **3** the O(P) atom is *trans* to chlorine. It thus appears that the iron–phosphoryl interactions in **3** are weaker.

Oxygen transfer from the nitrato complexes 2 *and* 3

The nitrato complexes **2** and **3** were found to be reluctant to react with olefins under anaerobic conditions. No reaction was observed between **2** or **3** and cyclohexene (in a 10 : 1 olefin : Fe ratio) after 72 h at room temperature under nitrogen: the unaltered nitrato complexes were quantitatively recovered.

On the other hand, they were found to react rapidly with phosphines even in the absence of oxygen. Thus, IR monitoring of the reaction between **3** and PPh_3 (4-fold excess) under nitrogen, in CH_2Cl_2, showed the rapid disappearance of the $\nu(NO_3)$ vibrations in **3** while $OPPh_3$ [$\nu(P{=}O) = 1188\ cm^{-1}$] became detectable. Treatment of the reaction mixture afforded, on the one hand (i) free $OPPh_3$ and (ii) the iron residue from which no definite species could be isolated. The IR spectrum of this residue showed no vibration in the 1850–1650 cm^{-1} region attributable to NO vibrations, while specific analysis indicated the presence of traces of NO_2 and no NO_3.

Complexes 2 *and* 3 *as catalysts in cyclohexene oxidation*

The nitrate complexes **2** and **3** are nevertheless catalysts in the oxidation of cyclohexene by molecular oxygen. They catalyse the aerobic oxidation of cyclohexene to mainly 2-cyclohexene-1-one and 2-cyclohexene-1-ol, cyclohexeneoxide being formed only in traces amounts (Table 3). These organic products were identified by GC-MS and their spectra compared with those of authentic samples.

The formation of cyclohexenone and cyclohexenol, which are typical autoxidation products of cyclohexene, suggests that compounds **2** and **3** are simply decomposing cyclohexenyl hydroperoxide, a classical behaviour for iron complexes.[14–16] Both compounds favour the cyclohexenone over cyclohexenol and this selectivity is increased on going from CH_2Cl_2 to CH_3CN as a solvent. Compound **3** in acetonitrile was found to induce the highest reactivities (36 moles of product per mole of complex at room temperature after 72 h) and selectivities (cyclohexenone : cyclohexenol = 68 : 30).

DISCUSSION

The ionic structure of $[Fe(Cl)_4][Fe(Cl)_2(OPN)_2]$, **1**, is maintained in the nitrato complex **2**, $[Fe(Cl)_4][Fe(NO_3)_2(OPN)_2]$, while further substitution of nitrate for chlorine in **1** resulted in the molecular $Fe(NO_3)_2(Cl)(OPN)$, **3**, where all iron

Table 3. O_2 Oxidation of cyclohexene catalysed by iron nitrates **2** and **3** at room temperature after 72 h[a]

Complex	Solvent	Distribution of the oxygenated products (%)			Alkene conversion (%)
		Epoxide	Alcohol	Ketone	
2	CH_2Cl_2	traces	36	64	25
2	CH_3CN	traces	33	67	32
3	CH_2Cl_2	1	38	61	25
3	CH_3CN	2	30	68	36

[a] Reaction conditions: O_2 (1 atm); [Fe] $= 2 \times 10^{-2}$ M; [cyclohexene]/[complex] = 100.

atoms are in the same environment. The stability of the $[Fe(Cl)_4]$ tetrahedron is most likely to be responsible for such a behaviour.

The molecular structure for **3** differs from that of the analogous $OPPh_3$ complex, $Fe(NO_3)_2(Cl)(OPPh_3)_2$, **4**,[2] as illustrated in Fig. 2. In compound **3**, both nitrato groups have their terminal N—O bond shorter than the two N—O bonds which involve the iron-coordinated oxygens; the internal O—N—O angle in the Fe—O—N≡O metallocycle is less than 120°. In marked contrast, we found that one of the nitrates in **4** contains a terminal N—O bond which is surprisingly long [1.311(0) Å], and, furthermore, much longer than both N—O(Fe) [1.074(0) and 0.985(0) Å] which, in turn, are shorter than usually observed in nitrato complexes.[13] It is noteworthy that, in **4**, the chlorine atom, quite unexpectedly, sits on an equatorial position with the two $OPPh_3$ at the apices of the pentagonal bipyramidal arrangement around iron. The bidentate nature of the OPN ligand and its bite prevent such configuration: the chlorine atom in **3** occupies an axial position with the OPN ligand spanning between equatorial and axial coordination sites.

These structural differences are of interest when considered with respect to the reactivities in oxidation of both compounds. Complex **4** was found to slowly epoxidize olefins.[2] Thus when compound **4** was kept in contact with cyclohexene (cyclohexene : Fe 10 : 1) under argon in CH_3CN solutions at room temperature, a 30% epoxide yield based on iron was obtained after 72 h while the nitrato groups in **4** were partly reduced to nitrosyls. Complex **3** was found not to react with olefins under these conditions, but to transfer the oxygens of its nitrates to a more oxophilic substrate such as a phosphine.

These results suggest that the presence of the electronegative chlorine ligand in the plane of the two nitrates of compound **4** might play an important role in the "abnormal" geometry of the nitrato group in **4** and, most importantly, in its easily transferable terminal oxygen atom. New iron nitrates with bidentate ligands LL′ capable of spaning the two axial positions in a $Fe(NO_3)_2Cl(LL')$ bipyramid are currently under study.

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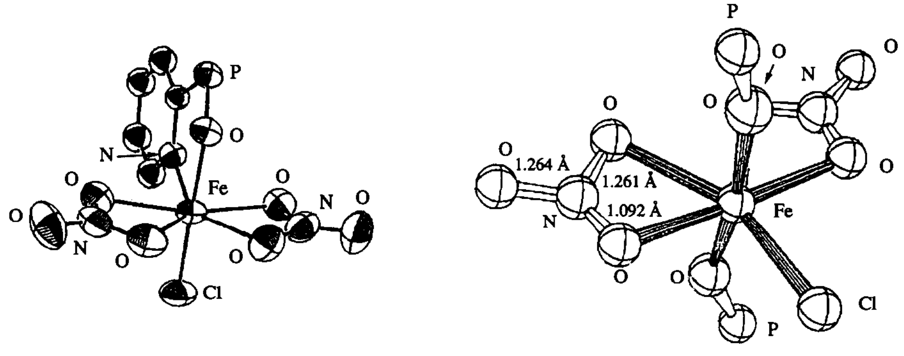

3 4

Fig. 2. Geometry of the nitrato complexes **3**, $Fe(NO_3)_2Cl(OPPh_2py)$ and **4**, $Fe(NO_3)_2Cl(OPPh_3)_2$.[2]

Supplementary materials available—Tables containing crystallographic data for **3**, final values of all refined atomic coordinates, thermal parameters, lists of observed and calculated structure factors and tables of bond distances and angles, torsional angles and least-square planes are available on request as supplementary material.

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