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New phosphathiamacrocycles containing polypypiridine units

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Abstract

A new 2,2'-bipyridine-based phosphadithiamacrocycle: 3,3'-5-phenyl-2,8-dithia-5-phospha[9]-2,2'-bipyridinophane (L) has been synthesized by reacting 6,6'-bis(bromomethyl)-2,2'-bipyridine and dilithium 3-phenyl-3-phosphapenta-1,5-dithiolate. The phosphoryl derivative: 3,3'-5-oxo-5-phenyl-2,8-dithia-5-phospha[9]-2,2'-bipyridinophane (Lox) synthesized by direct oxidation of L at open atmosphere. Both compounds have been isolated as white solids containing different amounts of LiBr.

The reaction of acetonitrile solutions of these solids with Fe(II) perchlorate gave the complexes $[FeBr(L)](ClO_4) \cdot 2H_2O$ and $[FeBr(Lox)](ClO_4) \cdot 3H_2O$, which were crystallized as $[FeBr(L)]Br \cdot H_2O$ and $[FeBr(Lox)](ClO_4) \cdot 1\frac{1}{6}$ MeOH salts from nitromethane or methanol, respectively. Both compounds were characterized by X-ray diffraction analysis. In both cases, a distorted octahedral environment is achieved at the Fe(II), with five sites occupied by the macrocycles L and Lox and the sixth by a monodentate bromine ligand. The bond distances found in the complex cation $[FeBr(Lox)]^+$ are compatible with a high-spin configuration. However, the same parameters for $[FeBr(L)]^+$ and their magnetic character are only compatible with a low-spin configuration. $(\bigcirc 2005 \text{ Elsevier Ltd. All rights reserved.})$

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1. Introduction

The chemistry of macrocyclic ligands containing phosphane groups as donor atoms has been less developed than those of their oxygen or nitrogen equivalents [1]. This fact has been mainly attributed to the air-sensitivity behavior of these compounds and the poor yields obtained in their preparations by high-dilution or template methods, although several high yield synthesis of homoleptic triphosphamacrocycles have recently been reported [2]. However, phosphathiamacrocycles seem to be more accessible as free ligands, and several examples can be found in the literature [3–6]. As a general trend, the interest in the chemistry of asymmetric phosphorus-sulfur donor ligands is mainly focused on the phenomenon of their hemilability and their potential use in catalytic processes [7,8]. Other possibilities are found when these P–S donor systems are integrated in macrocyclic systems, such as the documented ability of their phosphoryl [9,10], and thiophosphoryl [11] derivatives to interact selectively with ionic species that act as chemical sensors for anions.

On the other hand, the introduction of heteroaromatic subunits, such as bipyridine or 1,10-phenantroline into the macrocyclic structures generates different families of compounds which combine the special complexation features of these macrocycles [12] with the well-known photophysical, photochemical or electrochemical properties exhibited by the metal complexes of these heterocycles [13]. In this context, several 1,10-phenantroline containing polyaza and polythiamacrocycles have recently

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been reported and their complexing [14], luminescent [15] and sensing [16] properties studied.

Examples may be found of similar studies on polyaza and polyamidamacrocycles containing 2,2'-bipyridene units [14a,17], but less information is available on mono or polybipyridine-containing macrocycles [18], including the softer donor atoms.

As a part of our work in this field, we report herein on the synthesis of the new bipyridine-based phosphadithiamacrocycle: 3,3'-5-phenyl-2,8-dithia-5-phospha[9]-2,2'bipyridinophane (L) and their phosphoryl derivative: 3,3'-5-oxo-5-phenyl-2,8-dithia-5-phospha[9]-2,2'-bipyridinophane (Lox). The reactivity of these systems in the presence of Fe(II) salts is also investigated. At present, this is the first example of a phosphathmacrocycles containing polypyridine units.

2. Results and discussion

The synthetic pathway leading to the ligand L (Scheme 1) starts with the bromination of the 2-amino-6-picoline, followed by the reaction of the 2-bromo-6-picoline with Raney-Ni to afford the 6,6'-dimethyl-2,2'-bipyridine, which was finally halogenated with NBS to produce the 6,6'-bis(bromomethyl)-2,2'-bipyridine in an overall 10% yield [19,20]. Subsequent cyclisation of equimolar amounts of this dibromo derivative under high dilution conditions with the dilithium 3-phenyl-3-phosphapenta-1,5-dithiolate (obtained by previously reported methods [21]) produced low yields of the required macrocycle.

The ${}^{31}P{}^{1}H{}$ NMR spectrum of L shows a single signal at -21.29 ppm, which is in the range observed for similar dialkylarylphosphane-containing macrocyclic molecules [2d,5b,5d,22]. No additional downfield signals were observed, indicating that no phosphoryl or phos-



Scheme 1. Reagents and conditions: (i) NaNO₂ 1 M, Br₂ and HBr 98%; (ii) Ni-Raney, toluene; (iii) H₂O, 40 °C, 2 h; (iv) NBS, CCl₄, 3 h; (v) Ph–P(–CH₂–CH₂–S[–]Li⁺)₂, thf; (vi) stirring at open atmosphere, 24 h.

phonium derivatives are present in the final product obtained via this procedure.

The ¹H NMR spectrum displays a complex pattern due to the high inversion barrier of the phosphane group [23], which makes non-equivalent the geminal methylene protons. The S–CH₂-bipy protons appear as a pair of doublets centered at 4.0 ppm (AB system), and three groups of signals attributed to the —S–CH₂–CH₂–P– methylene protons coupled with the phosphorus atom are observed in the interval 2.4–3.1 ppm. The COSY spectrum shows coupling between three multiplets, which evidences that all four methylene protons and the phosphorus atom define an ABMNX system similar to those found in related macrocyclic molecules [24,6].

The ${}^{13}C{}^{1}H$ NMR spectrum shows a singlet for each different carbon atom in the molecule, split in some cases by the P-C coupling, thus indicating the conformational flexibility of the ligand L. The assignation of this spectrum was made on the basis of the literature data for the P-C coupling constants [25] and the observed chemical shifts of related phosphane macrocycles [5b,6]. Alkyl phosphanes are easily oxidized to their phosphoryl derivatives [26] and ligand L is no exception to this behavior. Exposing stirred chloroformic solutions of L to air yields almost quantitatively the phosphorylic macrocycle Lox. The patterns of the ¹H and ¹³C{¹H} NMR spectra of Lox are very similar to that described for L, whereas the ³¹P{¹H} NMR spectrum again shows a single signal at 37.21 ppm, which is in the expected position for a dialkyl aryl phosphine oxide [25,27].

The spectroscopic properties of the ligands L and Lox, including mass spectra, were consistent with the proposed structure; however, the elemental analyses of the two compounds were not coincident with those calculated from their empirical formulas. Taking into account that there was no spectroscopic evidence for the presence of additional organic compounds and no insoluble residues remained when L and Lox were dissolved in organic solvents, we proceeded with the study of their complexing abilities.

The reaction of the ligands L and Lox with equimolar amounts of hydrated Fe(ClO₄)₂ in a CH₂Cl₂-CH₃CN mixture affords red-purple microcrystalline materials corresponding to the respective iron (II) complexes. As in the case of the free ligands, elemental analysis of both complexes did not fit any empirical formula derived from simple metal to ligand to perchlorate counteranion relations. Hopefully, these complexes may easily crystallize, producing suitable materials for X-ray diffraction analysis, which could reveal (Figs. 1 and 2) the presence of the monocationic complex units $[1]^+$ and $[2]^+$, which contain one ligand (L and Lox, respectively), and one bromine atom bound to a Fe(II) atom in an octahedral environment. The presence of bromine in both compounds could only be explained if some of the LiBr generated in the synthesis of L is not completely removed by the purifica-



Fig. 1. Perspective view of the complex cation $[1]^+$ showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 2. Perspective view of complex cation $[2]^+$ showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

tion procedures used in the isolation of L and Lox. This assumption was confirmed by the Li analysis of both ligands using atomic emission spectrometry. The LiBr present in the Lox ligand can be easily removed by treating its chloroformic solutions with water. However, all the attempts made to purify L by the same or other procedures gave rise to its partial oxidation, and the separation of these L and Lox mixtures was unsuccessful. Furthermore, all attempts to synthesize Fe(II) complexes with the purified Lox ligand were also unsuccessful.

The complex cations $[1]^+$ and $[2]^+$ were initially obtained as purple microcrystalline perchlorate salts

showing a different degree of solubility in organic solvents. The $[1]^+$ perchlorate salt was sufficiently soluble in acetonitrile to be fully studied by NMR spectroscopy, a fact which reflects diamagnetic character, whereas the low solubility of $[2]^+$ perchlorate salt prevented further solution studies. The ³¹P{¹H} NMR spectrum of [1](ClO₄) shows a single signal at 132.52 ppm which suggests the presence of only one species in solution. These low-field shifts are characteristic of co-ordinated phosphanes in fused five-membered chelate rings [28] and several Fe(II)-triphosphamacrocyclic complexes showing similar shifts in the ³¹P NMR spectra have recently been reported [2a,2c]. Between 4.8 and 2.4 ppm, the ¹H NMR spectrum presents the same groups of multiplets, corresponding to the methylene protons found in the free ligand, but low-field shifted. However, the number of signals of the bipyridine rings increases with respect to the ligand L, which reflects the loss of the local symmetry by the effect of the co-ordination to the metal centre.

The ¹³C{¹H} NMR spectrum also shows the same number of signals as the free ligand, but in this latter case the most important differences are found in the region corresponding to the methylene groups, where the pair of doublets corresponding to the $-S-CH_2-CH_2-P$ - carbon atoms (22.4 and 33.5 ppm) appears high and low field displaced with respect to the L ligand (27.7 and 28.7 ppm). These data suggest that in solution the complex cation [1]⁺ maintains its monomeric character, which is in agreement with the well-known kinetic stability of the low-spin octahedral Fe(II) complexes [29].

The crystal structures of the L and Lox Fe(II) complexes, which crystallize as $[1]Br \cdot H_2O$ and $[2](ClO_4) \cdot 1\frac{1}{6}MeOH$ salts, showed the presence of the aforementioned $[1]^+$ and $[2]^+$ complex cations without significant interactions with the counter-anions and the solvate molecules. The diagrams for these complex cations are shown in Figs. 1 and 2, respectively. Crystallographic data for the structures are listed in Table 1; selected bond distances and angles for $[1]^+$ and $[2]^+$ are summarized in Tables 2 and 3, respectively.

As was mentioned above, the co-ordination geometry at the Fe(II) atoms in both complex cations is a distorted octahedron defined by the five donor atoms of the ligands and an additional bromine atom which is placed in a *trans* position with respect to the phosphorusphophane atom for $[1]^+$ or to the oxygen-phosphoryl atom for $[2]^+$. The major distortion in both octahedral environments is observed in the value of the S–Fe–S bond angles (105.30(6)° and 120.99(9)° for $[1]^+$ and $[2]^+$, respectively), and this can be attributed to the geometric constraint imposed by the simultaneous coordination of the two bipyridine nitrogen atoms and the two thioether sulfur atoms, thus defining three contiguous five-membered chelate rings. These four donor atoms and the metal ion are almost coplanar in

Table 1 Crystallographic data for $[1]Br \cdot H_2O$ and $[2](ClO_4) \cdot 1\frac{1}{6}MeOH$

	[1]Br · H ₂ O	$[2](\text{ClO}_4) \cdot 1\frac{1}{6}\text{MeOH}$
Formula	C22H25Br2FeN2OPS2	C23.17H27.67BrClFeN2O6.17-
		PS ₂
M	644.20	699.11
Crystal system	triclinic	trigonal
Space group	<i>P</i> 1 (no. 2)	$R\bar{3}$ (no. 148)
a (Å)	10.1594(15)	30.855(4)
b (Å)	14.376(2)	30.855(4)
c (Å)	9.2397(15)	16.083(4)
α (°)	92.537(15)	90
β (°)	110.820(12)	90
γ (°)	76.067(13)	120
$V(Å^3)$	1223.0(3)	13260(4)
Z	2	18
$T(\mathbf{K})$	294(2)	294(2)
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.749	1.576
$\mu ({\rm mm}^{-1})$	4.138	2.194
R_1^{a} $(I \ge 2\sigma(I))$	0.0397	0.0643
$wR_2^{\mathbf{b}} (I \ge 2\sigma(I))$	0.0962	0.1590
$a p = \sum \ E\ $	$ E /\sum E $	

 $WR_2 = \left[\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2\right]^{1/2}.$

Table 2 Selected bond distances (Å) and angles (°) for compound $[1]Br \cdot H_2O$

Br(1)–Fe	2.5108(9)
Fe–N(1)	1.918(4)
Fe-N(2)	1.921(4)
Fe–P	2.1780(13)
Fe–S(1)	2.2604(15)
Fe–S(2)	2.2667(14)
N(1)-Fe-N(2)	81.42(16)
N(1)–Fe–P	91.35(11)
N(2)–Fe–P	93.46(11)
N(1)-Fe-S(1)	86.71(13)
N(2)-Fe-S(1)	168.12(12)
P-Fe-S(1)	86.73(5)
N(1)-Fe-S(2)	167.92(13)
N(2)-Fe-S(2)	86.57(12)
P-Fe-S(2)	88.10(5)
S(1)-Fe-S(2)	105.30(6)
N(1)-Fe-Br(1)	93.52(11)
N(2)-Fe-Br(1)	93.28(10)
P–Fe–Br(1)	172.21(4)
S(1)–Fe–Br(1)	87.49(4)
S(2)–Fe–Br(1)	88.40(4)

the complex cation $[1]^+$ whereas in $[2]^+$ the iron atom deviates 0.191(2) Å from the N₂S₂ plane.

The Fe–Br bond distances observed for both complexes are similar (2.5108(9) and 2.4887(15) Å for $[1]^+$ and $[2]^+$, respectively), and lie in the same range as those reported for related octahedral Fe(II) complexes containing non-bridging bromine ligands [30]. This situation is similar for the Fe–O(phosphoryl) bond distance in $[2]^+$, which shows a value (2.107(5) Å) comparable to that observed in the few reported structures containing octahedral Fe(II) complexes with coordinated phosphoryl ligands [31]. However, the Fe–P(phosphine)

Table 3

Selected bond distances (Å) and angles (°) for compound $[2](C[O_4) \cdot 1 \stackrel{1}{\to} MeOH$

Br–Fe	2.4887(15)
Fe–O(1)	2.107(5)
Fe-N(2)	2.113(7)
Fe–N(1)	2.134(7)
Fe-S(1)	2.558(3)
Fe–S(2)	2.579(3)
P–O (1)	1.502(5)
O(1)-Fe-N(2)	86.3(2)
O(1)-Fe-N(1)	84.9(2)
N(2)-Fe- $N(1)$	77.5(3)
O(1)–Fe–Br	167.55(15)
N(2)–Fe–Br	102.41(8)
N(1)–Fe–Br	105.56(18)
O(1)-Fe-S(1)	86.00(15)
N(2)-Fe-S(1)	156.9(2)
N(1)-Fe-S(1)	80.1(2)
Br–Fe–S(1)	89.07(7)
O(1)-Fe-S(2)	84.55(16)
N(2)-Fe-S(2)	79.9(2)
N(1)-Fe-S(2)	155.5(2)
Br–Fe–S(2)	88.23(7)
S(1)–Fe–S(2)	120.99(9)
P–O(1)–Fe	124.3(3)

bond distance for $[1]^+$ (2.1780(13) Å) is somewhat less when compared with those observed in other low-spin Fe(II) complexes with aryl-dialkyl phosphines [32,33].

The Fe–N(bipyridine) distances for $[1]^+$ (1.918(4) and 1.921(4) Å) are also slightly less than the average Fe–N bond length (ca. 2.00 Å) obtained through a Cambridge Crystallographic Data Base (CCDB) search [34] on octahedral Fe(II) complexes containing bipyridine as ligand and covering 47 structures. However, the same distances for $[2]^+$ (2.134(7) and 2.113(7) Å) are ca. 0.20 Å longer than those found in $[1]^+$ and similar to those reported for related octahedral high-spin Fe(II)-bipyridine complexes [35]. The same trends are also observed for the Fe–S(thioether) distances, which in the case of $[1]^+$ (2.2604(15) and 2.2667(14) Å) are very close to the Fe-S bond lengths observed in low-spin Fe(II) complexes of homoleptic polythiamacrocycles [36] and azathiamacrocycles [37] whereas in the complex cation $[2]^+$ these distances are noticeably longer (2.558(3) and 2.579(3) Å)and similar to those reported for high-spin Fe(II) complexes with different thioether containing ligands [32,38]. These structural data confirm the low-spin nature of the Fe(II) metal ion in the complex $[1]^+$. However the bond distances and angles in the complex cation $[2]^+$ are only compatible with a high-spin electronic configuration for the Fe(II) metal ion, a fact that can be attributed to the increase in the macrocyclic ligand hardness when the phosphane group in L is replaced by their phosphoryl derivative. Only the Br–Fe distance is slightly short in $[2]^+$ than in $[1]^+$, which may be due to the *trans*-effect of the P(phosphane) atom in $[1]^+$ in comparison with the O(phosphoryl) atom in [2] [2].

3. Experimental

The syntheses were carried out using standard Schlenk techniques under dry dinitrogen atmosphere. The solvents were dried by conventional methods and distilled under dinitrogen before use. Dilithium 3-phenyl-3-phosphapenta-1,5-dithiolate and 6,6'-bis(bromomethyl)-2,2'-bipyridine [20,21] were prepared according to published procedures. Chemical analyses were performed in the Chemical Analysis Service of the Universitat Autònoma de Barcelona. Elemental analyses were carried out using a Carlo Erba EA-1108 instrument. Li determinations were made by atomic emission spectrometry (AES) using a Perkin-Elmer 2100 instrument; the samples were previously prepared treating them with HNO₃/H₂O (1:1) at 180 psi during 40 min in a microwaves digestor (CEM2000). The NMR spectra were run in the NMR Service of the Universitat Autònoma de Barcelona. ¹H and ¹³C $\{^{1}H\}$ NMR spectra were recorded using a Bruker 400 MHz AM instrument and the ${}^{31}P{}^{1}H$ NMR spectra were recorded using a Bruker 250 MHz AC instrument with chemical shifts given as ppm relative to 85% H₃PO₄. COSY and HNQC experiments were made in order to assign the ¹H and ¹³C spectra by using general standard parameters. Mass spectra were recorded using a HP298S GC/ MS system.

4. Syntheses

4.1. 3,3'-5-phenyl-2,8-dithia-5-phospha[9]-2,2'bipyridinophane (L)

Under a dinitrogen atmosphere, a solution of dilithium 3-phenyl-3-phosphapenta-1,5-dithiolate in thf (100 cm³, 0.09 M) and a solution of 6,6'-bis(bromomethyl)-2,2'-bipyridine (3.10 g, 9 mmol) in thf (100 cm^3) were added simultaneously to thf (500 cm^3) over a period of 5 h at room temperature. After the addition, the mixture was stirred for a further 48 h. The thf was removed under vacuum and the resulting oily yellow residue was extracted with diethyl ether $(3 \times 60 \text{ cm}^3)$. The ethereal layer was separated, evaporated under vacuum, and the residue was dissolved in the minimum amount of CH₂Cl₂. After slow addition of petroleum ether $(40-60^{\circ})$ to this solution a white precipitate appeared which was filtered off and vacuum dried. Yield (calculated for L · 2LiBr) 0.54 g, 10%. Anal. Calc. for C₂₂H₂₃N₂PS₂Li₂Br₂: C, 45.23; H, 3.97; N, 4.79; S, 10.98; Li, 2.38. Found: C, 44.4; H, 3.8; N, 4.1; S, 10.2%; Li (determined by AES), 21.7 mg Li/1 g sample, 2.2%. ¹H NMR (400 MHz, CDCl₃): δ 2.07 (m, 2, -S-CH₂-CH₂-P-), 2.45 (m, 2, -S-CH₂-CH₂-P-), 2.84 (m, 4, -S-CH₂-CH₂-), 3.90 (d, 2, -S-CH₂-Ph, J = 13.9 Hz), 4.02 (d, 2, -S-CH₂-Ph, J = 13.9 Hz),

7.42–7.77 (m, 11, Ar). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 27.71 (d, S–CH₂–CH₂–P–, J = 10.5 Hz), 28.72 (d, –S–CH₂–CH₂–P–, J = 20.9 Hz), 37.92 (–S–CH₂–Ph), 119.32, 124.62, 139.31 (Bipy), 128.08 (d, P–Ph, J = 7.0 Hz), 128.54 (d, P–Ph, J = 15.7 Hz), 131.45 (d, P–Ph, J = 19.2 Hz), 131.86 (d, P–Ph, J = 19.4 Hz), 152.45, 158.58 (Bipy). ³¹P{¹H} NMR (101 MHz,

4.2. 3,3'-5-oxo-5-phenyl-2,8-dithia-5-phospha[9]-2,2'bipyridinophane (Lox)

CDCl₃): $\delta - 21.29$. Mass spectrum (EI); m/z 410 (M^+).

A solution of L·2LiBr (0.200 g, 0.34 mmol) in $CHCl_3$ (30 cm³) was stirred at open atmosphere and room temperature for 24 h. The resulting solution was evaporated to dryness and the resulting solid collected. Yield (calculated for Lox · 2LiBr) 0.198 g, 97%. Anal. Calc. for C₂₂H₂₃N₂OPS₂Li₂Br₂: C, 44.02; H, 3.86; N, 4.67; S, 10.68; Li, 2.31. Found: C, 43.8; H, 3.4; N, 4.6; S, 10.3%; Li (determined by AES), 24.8 mg Li/1 g sample, 2.5%. ¹H NMR (400 MHz, CDCl₃): δ 2.35 (m, 2, -S-CH₂-CH₂-P-), 2.80 (m, 6, -S-CH₂-CH₂-P-), 3.81 (d, 2, $-S-CH_2-Ph$, J = 13.9 Hz), 3.92 (d, 2, $-S-CH_2-$ Ph, J = 13.9 Hz), 7.38–7.89 (m, 11, Ar). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 30.98 (d, -S-CH₂-CH₂-P-, J = 14.8 Hz), 31.95 (d, S-CH₂-CH₂-P-, J =18.5 Hz), 36.27 (-S-CH₂-Ph), 120.60, 123.66 (Bipy), 128.81 (d, P-Ph, J = 11.09 Hz), 130.09 (d, P-Ph, J = 9.2 Hz), 130.50 (d, P-Ph, J = 9.4 Hz), 132.04 (s, P-Ph), 138.78, 138.93, 160.46 (Bipy). ³¹P{¹H} NMR (101 MHz, CDCl₃): δ 37.21. Mass spectrum (EI); m/z426 (M^+) .

4.3. $[FeBr(L)](ClO_4) \cdot 2H_2O \cdot [1](ClO_4) \cdot 2H_2O$

A solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (44 mg, 0.122 mmol) in acetonitrile (5 cm^3) was slowly added to a solution of L · 2LiBr (50 mg, 0.086 mmol) in dichloromethane (2 cm^3) . The solution changed immediately to red-purple and a solid of the same colour appeared which was filtered off, washed with dichloromethane and vacuum dried. Yield: 17 mg, 29%. Anal. Calc. for C22H27BrCl-FeN₂-O₆PS₂: C, 38.76; H, 3.99; N, 4.11; S, 9.45. Found: C, 38.9; H, 3.6; N, 4.2; S, 9.3%. ¹H NMR (400 MHz, CD₃NO₂): δ 2.37 (m, 4, -S-CH₂-CH₂-P-), 3.13 (m, 4, $-S-CH_2-CH_2-P-$), 4.67 (d, 2, $-S-CH_2-Ph$, J = 18.0 Hz), 4.81 (d, 2, $-S-CH_2-Ph$, J = 18.0 Hz), 6.24–7.00 (m, 6, Bipy), 7.78 (m, 5, P–Ph). ¹³C{¹H} NMR (100 MHz, CD₃NO₂): δ 22.51 (d, -S-CH₂-CH₂-P-, J = 29.7 Hz), 33.41 (d, S-CH₂-CH₂-P-, J = 31.5 Hz), 44.36 (-S-CH2-Ph), 117.18, 117.56 (Bipy), 128.81 (d, P-Ph, J= 11.09 Hz), 124.42 (d, P–Ph, J = 8.9 Hz), 124.89 (d, P– Ph, J = 9.1 Hz), 126.53 (s, P-Ph), 130.41, 153.59, 159.14 (Bipy). ${}^{31}P{}^{1}H{}$ NMR (101 MHz, CDCl₃): δ 132.52.

4.4. $[FeBr(Lox)](ClO_4) \cdot 3H_2O \cdot [\mathbf{2}](ClO_4) \cdot 3H_2O$

The compound was prepared as for [1](ClO₄) \cdot 2H₂O using Lox as ligand. Yield: 19 mg, 29%. *Anal.* Calc. for C₂₂H₂₉BrClFeN₂O₈PS₂: C, 36.92; H, 4.08; N, 3.91; S, 8.96. Found: C, 36.4; H, 3.9; N, 3.8; S, 8.2%.

5. Crystallography

The slow evaporation of a nitromethane solution of [1](ClO₄) · 2H₂O and a methanol solution of [2](ClO₄) · 3H₂O produced crystalline materials corresponding to [1]Br · H₂O and [2](ClO₄) · 1 $\frac{1}{6}$ MeOH, respectively. Singlecrystal data were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo K α radiation. The unit cell parameters for both compounds were determined by least-squares refinement of 25 carefully centered reflections. All data obtained were corrected for empirical absorption (P scan). A total of 4563 and 5557 reflections giving 4296 and 5198 unique reflections ($R_{int} = 0.0179$ and 0.0562) were collected by T/2 scan mode ($2\theta_{max} = 50^{\circ}$) for [1]Br · H₂O and [2](ClO₄) · 1 $\frac{1}{6}$ MeOH, respectively.

Both structures were solved by direct methods and least-squares refinements were performed using the SHELX-97 program system [39]. For [1]Br \cdot H₂O non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at the fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters.

The asymmetric unit of $[2](ClO_4) \cdot 1\frac{1}{6}$ MeOH consists of the complex unit $[2]^+$, disordered perchlorate ion, one methanol molecule at common position and 1/6 of disordered methanol molecule at threefold axis. The perchlorate ion shows rotational disorder, the Cl–O(2) bond being common shared by both rotamers. The disordered oxygen atoms of the perchlorate ion and the methanol molecules were refined with isotropic displacement parameters; the rest of the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of the methanol molecules could not be reliably positioned but the remainder of the hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms by using the SHELX-97 default parameters.

6. Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request. CCDC Nos.: 274557 and 274558 for [1]Br \cdot H₂O and [2](ClO₄) \cdot 1 $\frac{1}{6}$ MeOH, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)

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