Hetero trinuclear oxo-bridged complexes of ruthenium porphyrin and iron phthalocyanine

Fabio Zobi and Dennis V. Stynes

Abstract: New diamagnetic hetero bi- and trinuclear oxo-bridged metal complexes of formula (L)(Pc)Fe-O-Ru(TPP′)(O) and (L)(Pc)Fe-O-Ru(TPP′)-O-Fe(Pc)(L) have been prepared from Ru(TPP′)$(O)_2$ and Fe(Pc)$(L)_2$ (TPP′ = tetrakis(4-methoxyphenyl)porphyrinate, Pc = phthalocyanate ion, L = monodentate ligand). The trinuclear complex binds a variety of ligands (4,4′-bipy, 4-MePy, $P(OEt)_3$, pip, NH_3, 1-MeIm, $P(Me)_2Ph$) *trans* to the oxo-bridge. ^1H NMR spectra are characterized by large ring current shifts (rcs) due to the TPP′ and Pc ions. The complexes show an unusually weak Pc Q band in their visible spectra at 700 nm and two CT bands in the near-IR region from 1000 to 1500 nm, which are sensitive to the *trans* ligand. The trinuclear complex can be reversibly oxidized to the +1 and +2 ions, formally Fe(IV)-O-Ru(IV)-O-Fe(III) and Fe(IV)-O-Ru(IV)-O-Fe(IV) at 0.4 and 0.76 V. The +1 ion is chemically obtained by reaction of the neutral species with $(Cp)_2Fe^+$ for L = 4-MePy and this reaction is reversed upon addition of L′ = $P(Me)_2Ph$. Reductive cleavage by hydroquinone, phosphines and phosphites are the slowest of all RuTPP$[O(FeN_4)]_2$ systems studied to date ($t_{1/2}$ = 8 h at 40°C).

Key words: ruthenium, iron, porphyrin, phthalocyanine, oxo.

Résumé : En faisant réagir du Ru(TPP′)$(O)_2$ et du Fe(Pc)$(L)_2$ (TPP′ = tétrakis(4-méthoxyphényl)porphyrinate, Pc = ion phtalocyanate, L = ligand monodentate), on a préparé de nouveaux complexes métalliques diamagnétiques, hétéro-bi et -trinucléaires, à ponts oxo, de formules (L)(Pc)Fe-O-Ru(TPP′)(O) et (L)(Pc)Fe-O-Ru(TPP′)-O-Fe(Pc)(L). Le complexe trinucléaire se fixe à une variété de ligands (4,4′-bipy, 4-MePy, $P(OEt)_3$, pip, NH_3, 1-MeIm, $P(Me)_2Ph$), de façon *trans* par rapport au pont oxo. Les spectres de RMN du ^1H sont caractérisés par d’importants déplacements de courant de cycle causés par les ions TPP′ et Pc. Dans leurs spectres dans le visible, ces complexes comportent une bande Q anormalement faible pour le Pc, à 700 nm, et deux bandes CT dans la région du proche infrarouge, entre 1000 et 1500 nm, qui sont sensibles au ligand *trans*. À des valeurs de 0,4 et 0,76 V suivant le cas, le complexe trinucléaire peut être oxydé de façon réversible vers les ions +1 et +2 qui sont formellement le Fe(IV)-O-Ru(IV)-O-Fe(III) et le Fe(IV)-O-Ru(IV)-O-Fe(IV). On peut obtenir l’ion +1 de façon chimique par réaction de l’espèce neutre avec $(Cp)_2Fe^+$, pour L = 4-MePy, et cette réaction est renversée par l’addition de L′ = $P(Me)_2Ph$. De tous les clivages réducteurs par l’hydroquinone, les phosphines et les phosphites observés à date avec des systèmes RuTPP$[O(FeN_4)]_2$, ce sont les plus lents ($t_{1/2}$ = 8 h, à 40°C).

Mots clés : ruthénium, fer, porphyrine, phtalocyanine, oxo.

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Introduction

The study of oxo-bridged multinuclear metal complexes has continued to attract interest both for their biological relevance (1) and as the most common example of single atom bridged systems (2). Oxo-bridged metal complexes have been prepared by hydrolytic processes (3), by one-electron redox reactions in which a high valent metal-oxo compound is reacted with a lower valent metal complex (4), and by autoxidation (5). We and others have employed a $Ru^{VI}(O)_2$ porphyrin as a route to μ-oxo trinuclear species (6, 7) In this study we extend this reaction to a new class of oxo-bridged heterotrinuclear complexes containing the iron phthalocyanine (FePc) moiety.

Experimental

Materials

Common ligands were obtained from standard sources and were used as received. Solvents were distilled and kept over molecular sieves (3 Å). $CDCl_3$ was dried over activated molecular sieves (3 Å) and freed of acid by filtering through vacuum dried $Al(OH)_3$. Tetrakis(4-methoxyphenyl) porphyrin (H_2TPP′), Ru(TPP′)(CO)(C_2H_5OH), and Ru(TPP′)$(O)_2$ were prepared by literature methods (8–10).

Physical measurements

Visible spectra were recorded on a HP-8451 Diode array UV–vis spectrometer in 1 cm glass cuvettes thermostated at 25°C. ^1H NMR spectra were obtained on a Bruker ARX 400 MHz spectrometer at 300 K using $CDCl_3$ as the solvent

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Dedicated to Professor Brian James on the occasion of his 65th birthday.

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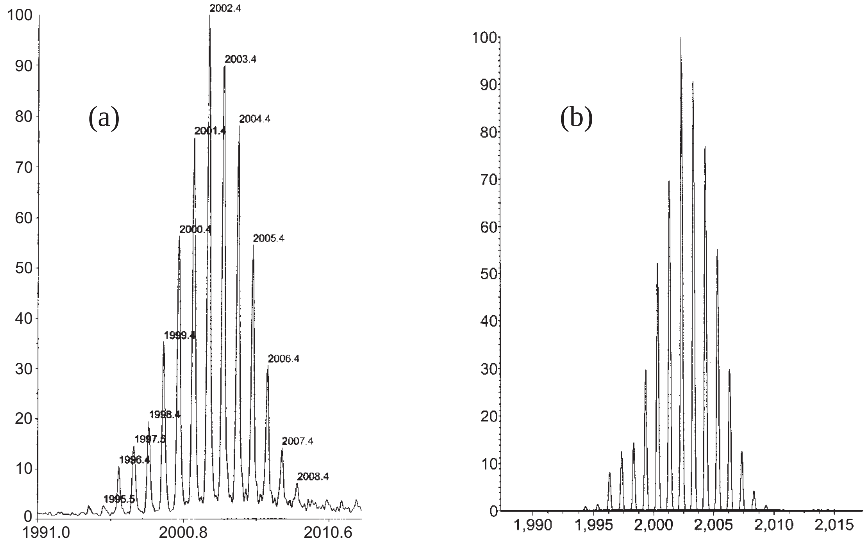
Fig. 1. Experimental (*a*) and simulated (*b*) MS spectra of **2**. Shown is the isotopic distribution of the peak at *m*/*z* 2002, assigned to the $[(Pc)FeO]_2Ru(TPP')$ skeleton.



with TMS as an internal standard. Near-IR spectra were recorded on a Cary 2400 UV–vis – near-IR spectrometer at 25°C. Electrochemical data were collected with a computer-controlled Electroanalytical Cypress System model CS-1090. Cyclic voltammetry experiments were performed under a nitrogen atmosphere in a CH_2Cl_2 solution containing 0.1 M $(TBA)PF_6$ and ~5 × 10^{-3} M complex at –42°C. A platinum disk sealed in glass was used as a working electrode. Graphite was used as a counter electrode and AgCl/Ag was used as the reference electrode. Ferrocene was used as an internal reference (Fc+/Fc = 0.46 V in CH_2Cl_2 vs. SCE). Mass spectra were collected with a Perseptive Biosystems MALDI spectrometer, model Voyager-DE STR operating in the positive-ion mode.

Fe(Pc)(L)$_2$ (L = 4-MePy, 1-MeIm)

Fe(Pc) (Pc = phthalocyanate ion) (Aldrich) (1 g, 1.76 mmol) was dissolved in a $CHCl_3$ solution (25 mL) containing 4-MePy (5 mL, 51.4 mmol). After stirring the solution for 10 h at room temperature a purple crystalline precipitate was collected by filtration through paper. The product was then washed with hexane and dried in vacuo. Yield: 579 mg, 44%. $Fe(Pc)(1\text{-}MeIm)_2$ was prepared by a similar procedure. Yield: 697 mg, 54%.

[(1-MeIm)Fe(Pc)O]Ru(TPP′)(O) (1)

Freshly made $Ru(TPP')(O)_2$ (5 mg, 5.8 × 10^{-3} mmol) and $Fe(Pc)(1\text{-}MeIm)_2$ (10 mg, 1.36 × 10^{-2} mmol) were dissolved in a N_2 purged $CDCl_3$ solution (5 mL) and the reaction followed by NMR. When all $Ru(TPP')(O)_2$ had reacted (indicated by the disappearance of the H_β peak at 9.11 ppm) the reaction was quenched by slowly adding hexane (10 mL). The ppt was filtered through paper and dried in vacuo. Yield: 6.9 mg, 80%. The complex was very reactive and it formed an insoluble precipitate both in solution (within minutes) and in the solid state even when stored in vacuo at –20°C.

[(4-MePy)Fe(Pc)O]$_2$Ru(TPP′) (2)

Freshly made $Ru(TPP')(O)_2$ (100 mg, 0.116 mmol) and $Fe(Pc)(4\text{-}MePy)_2$ (200 mg, 0.265 mmol) were mixed as solids and dissolved in a CH_2Cl_2–$CHCl_3$ solution (3:1, 18 mL). After 40 min hexane (50 mL) was slowly added depositing 223 mg of a black crude precipitate. The product was found to be contaminated by unreacted $Fe(Pc)(4\text{-}MePy)_2$ and $[Ru(TPP')(OH)]_2O$, which were subsequently removed by recrystallizing the complex from a hexane–$CHCl_3$ solution. Yield: 199 mg, 79%. MALDI-MS ($CHCl_3$) *m*/*z*: 2188 ($[M]^+$). Other relevant peaks are at 2002 ($[(PcFeO)_2Ru(TPP')]^+$) (Fig. 1), 1418 ($[(Pc)FeORu(TPP')]^+$), 850 ($[Ru(TPP')(O)]^+$), 662 ($[Fe(Pc)(4\text{-}MePy)]^+$), 569 ($[Fe(Pc)]^+$). Anal. calcd for $C_{124}H_{82}N_{22}O_6Fe_2Ru$: C 68.04, H 3.78, N 14.08; found: C 68.39, H 3.76, N 13.91. This complex is sensitive to trace acid normally present in $CDCl_3$, therefore, its ^{1}H NMR spectrum must be taken in acid free solvents. Various ligated derivatives of **2** were generated in situ in a NMR tube by addition of excess ligand L (L = 4,4′-bipy, pip, NH_3, 1-MeIm, $P(CH_3)_2Ph$) to the 4-MePy-ligated derivative in a chloroform solution. Solid samples were obtained in quantitative yields by precipitation with hexane (typically 1–3 mg).

Kinetic measurements

Neat phosphines, phosphites, or a dichloromethane solution of hydroquinone were injected via syringe into a thermostated (40°C) $CHCl_3$ solution of the complex (1 × 10^{-5} M) and the subsequent reaction followed by visible spectroscopy. Pseudo-first-order rate constants were obtained by monitoring the growth of the Soret band of the $Ru(TPP')L_2$ complex. Spectra were typically scanned between 380 and 820 nm under anaerobic conditions.

Fig. 2. Reaction sequence in the formation of [(4-MePy)Fe(Pc)O]2Ru(TPP′) (**2**). The intermediate binuclear species is indicated by **1**.

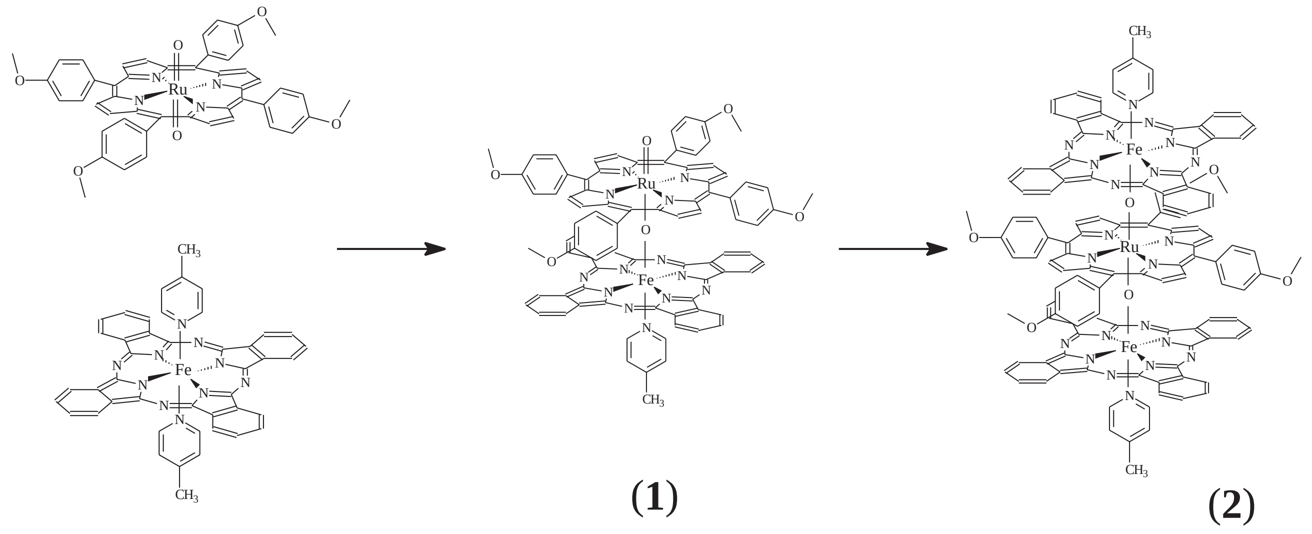
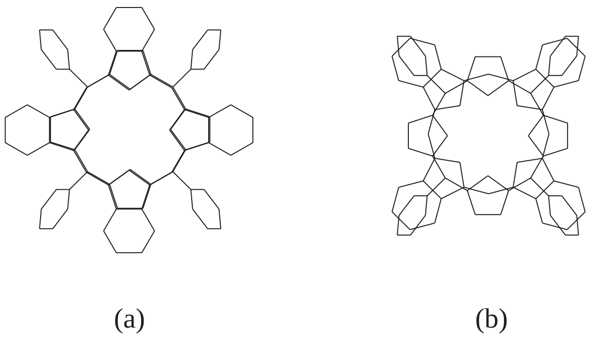


Fig. 3. Eclipsed (*a*) and staggered (*b*) conformations of stacked TPP and Pc rings. A staggered conformation leads to prohibited contacts between Pc benzopyrrole rings and TPP phenyls.


(a) (b)

Results and discussion

Synthesis

Formation of **2**, the trinuclear complex, proceeds through the initial formation of a reactive binuclear species **1** (Fig. 2). Both steps involve an inner-sphere oxidation of the Fe^{II} metal center by the dioxo Ru-porphyrin. Attempts to isolate the 4-MePy derivative of **1** proved unsuccessful as **1**-(4-MePy) is extremely reactive.

The 1-MeIm derivative was isolated but survives only long enough to obtain an NMR and observe its reactions with reductants. Oxidation of the Fe^{II} metal center by $Ru(TPP')(O)_2$ requires a vacant coordination site on Fe(Pc). Ligand dissociation in $Fe(Pc)(1\text{-}MeIm)_2$ is about 50 times slower than $Fe(Pc)(4\text{-}MePy)_2$ (11) and this allows for a better control over the reaction. Slow dissociation of 1-MeIm in the binuclear complex may also retard polymerization of **1**. While **1**-(4-MePy) is generated in situ by reacting $Ru(TPP')(O)_2$ with $Fe(Pc)(4\text{-}MePy)_2$ in a 1:1 ratio, an excess of $Fe(Pc)(1\text{-}MeIm)_2$ was used in the slower formation of **1**-(1-MeIm) to avoid formation of the $[Ru(TPP')(OH)]_2O$ dimer.

The binuclear complex is formally Fe^{IV}-O-Ru^{IV} and is the first example of a Ru porphyrin complex containing both a terminal and a bridging oxo ligand. The presence of the reactive terminal oxygen is inferred from the observation that the binuclear species reacts with a second Fe(Pc) unit to form the trinuclear compound and undergoes rapid reactions on mixing with hydroquinone, DMSO, or dimethylphenylphosphine. The oxidation products quinone, $DMSO_2$, and dimethylphenylphosphine oxide, respectively, were identified in the NMR spectrum.

^1H NMR spectra

Both **1** and **2** are diamagnetic as expected for linear species with axial d_π^4 and d_π^8 configurations (6). ^1H NMR provides definitive characterization of the different ligated bi- and trinuclear μ-oxo species. All spectra are characterized by large ring current shifts (rcs) due to the TPP′ and Pc ions. Observed shifts are consistent with rcs calculations carried out on the basis of Abraham 12-loop model (12). An eclipsed conformation of the macrocycles is most consistent with the NMR data as this places the porphyrin H_β protons directly over the benzopyrrole rings. A staggered conformation would lead to prohibited contacts with the TPP′ phenyls (Fig. 3). An eclipsed structure is rare for X-bridged dimers and trimers (X = C, N, O). The only other known examples are $[(THF)(TPP)Fe\text{-}N\text{-}Fe(Pc)(H_2O)](I_5)$ (13), $[(Pc)Al]_2O$ (14), and $[Fe(OEP)]_2O$ (15). Complex **2** is the first example of a fully eclipsed macrocyclic trinuclear.[2]

^1H NMR spectra of the bi- and trinuclear complexes are shown in Figs. 4*a* and *b*, respectively. The binuclear species is identified on the basis of differentiated TPP′ phenyls protons. Phenyl protons directed toward the Fe(Pc) face project into the deshielding region of the Pc ring and experience a downfield shift, while those directed to the open face (denoted $H_{o'}$ and $H_{m'}$ in Fig. 4*a*) experience a small upfield shift. In the centrosymmetric trinuclear species a single set of ortho and meta phenyl resonances is observed (H_o and H_m in Fig. 4*b*). The porphyrin H_β protons are shifted upfield (rela-

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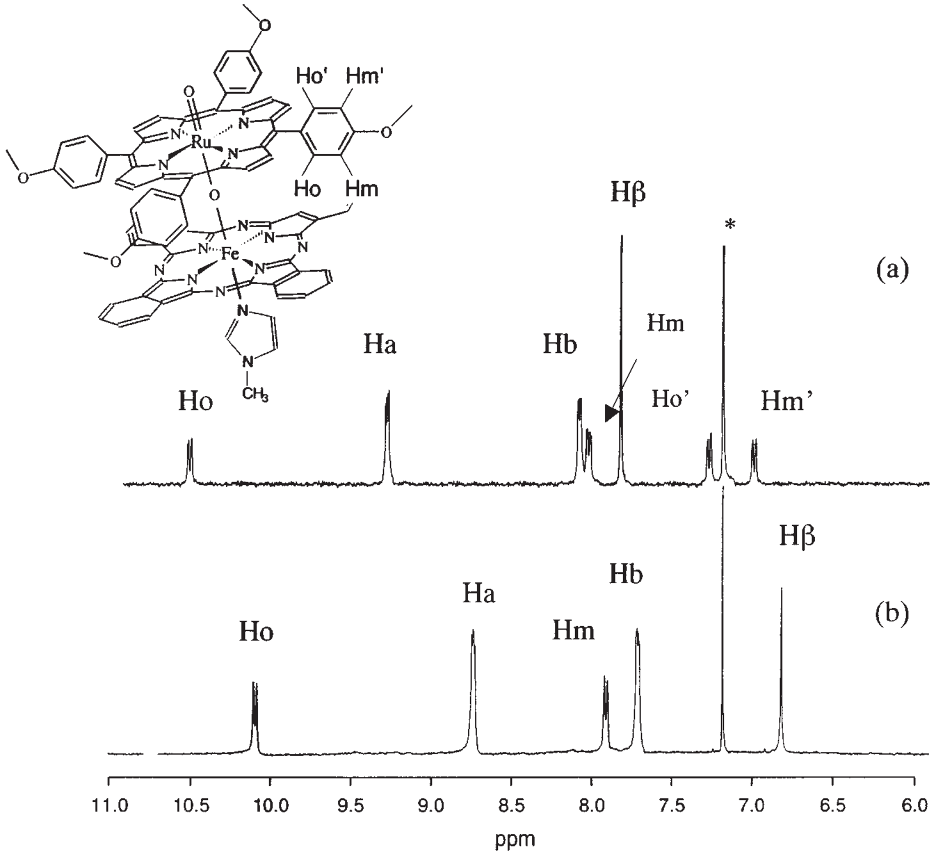
[2] The $[Mo_3O_4(TPP)_3]^+$ ion shows partial eclipse of two Mo(TPP) moieties (16).

Fig. 4. Aromatic region of ^{1}H NMR spectra of (*a*) binuclear **1**-(1-MeIm); and (*b*) trinuclear **2**-(4-MePy)$_2$ species in $CDCl_3$ (* indicates solvent peak).



tive to Ru(TPP′)(O)$_2$) in both **1** and **2**. Axial ligand resonances are also shifted upfield as a result of the cumulative effect of Pc and TPP′ rcs. Hydrogen atoms at the *ortho* position in 4-MePy, for example, suffer a 8.5 ppm upfield shift in **1** and over 9 ppm upfield shift in **2** when compared to the free ligand. Spectral data are collected in Table 1.

Electronic spectra

The visible spectrum of **2** is given in Fig. 5. It shows a typical porphyrin Soret band at 410 nm in contrast to a red-shifted Soret band at about 435 nm in DMG and DPG trinuclears (6). A weak bathochromic shifted phthalocyanine Q band at about 700 nm is present in the visible spectrum of **2**. An unusually weak Pc Q band is also reported for the μ-nitrido (TPP)Mn-N-Fe(Pc) (17) and the μ-oxo (TPP)Cr-O-Fe(Pc) (18) complexes. This feature may be characteristic of X-bridged metal atoms containing face-to-face Pc and porphyrin rings. Additionally, two low energy charge transfer bands (CT1 and CT2) appear in the near-IR region at 1050 and 1330 nm (see Fig. 6 and Table 2).

The CT bands show significant shifts as a function of the axial ligand suggesting that MO's with substantial iron character are involved. The two bands are tentatively assigned to an oxo-to-metal (CT1) and to an intervalence metal-to-metal charge transfer (CT2). A similar assignment was made in DMG based systems (6). The lower oxidation potential of **2** translates in a smaller HOMO–LUMO gap and less energy is required for this transition. Consequently CT2 in **2** shifts 500 nm and is well-resolved in the IR. The same is true for CT1 (see Tables 3 and 4). Both CT bands undergo a bathochromic shift with increasing π-acceptor strength and (or) increasing basicity of the axial ligand. A typical change is shown in Fig. 6.

Ligation

The Fe(Pc) based heterotrinuclear complexes are substantially more stable in solution than borylated dioxime and paramagnetic heme or Fe(Schiff base)-derived Fe-O-Ru-O-Fe systems (6, 7). Ligand displacement at the Fe^{III} center can be followed at room temperature by both NMR and near-IR spectroscopy. 4-MePy in **2** is easily displaced by stonger σ-donors such as NH_3 and 1-MeIm, by π-acid ligands including P(Me)$_2$Ph, and by ligands capable of promoting chain elongation like 4,4′-bipy (eq. [1]). These substitution reactions are over on mixing at ambient temperature but are in the slow exchange limit in the ^{1}H NMR.

$$[1] \qquad [(4\text{-MePy})Fe(Pc)O]_2Ru(TPP') + 2L' \rightarrow [(L')Fe(Pc)O]_2Ru(TPP') + 2(4\text{-MePy})$$

The relative binding strength of the different ligands was obtained from spectrochemical titrations in the near-IR and follows the order:

$$4,4'\text{-bipy} < 4\text{-MePy} \sim P(OEt)_3 < \text{pip} < NH_3 < 1\text{-MeIm} < P(CH_3)_2Ph$$

Table 1. ${}^1H$ NMR data (δ, ppm) in $CDCl_3$.

Complex	H_β	H_o	H_m	OCH_3	H_a	H_b	Ligand
2-(4-MePy)$_2$	6.89	10.18	8.00	4.59	8.82	7.80	${}^LH_o$ –0.90, ${}^LH_m$ 3.59, ${}^LCH_3$ 0.30
2-(1-MeIm)$_2$	6.88	10.15	7.97	4.58	8.80	7.77	H_2 –1.05, H_4 –0.61, H_5 3.31, CH_3 0.88
2-[P(Me$_2$Ph)]$_2$	6.81	10.00	7.92	4.54	8.67	7.70	Hα 2.60, Hβ 5.30, Hγ 6.00, CH_3 –4.12
2-(NH$_3$)$_2$	6.78	10.00	7.92	4.53	8.76	7.78	NH_3 –9.00
2-[P(OEt)$_3$]$_2$	6.84	10.10	7.93	4.55	8.76	7.69	CH_3 –1.29, CH_2 –0.36
2-(4-MePy)[P(OEt)$_3$]	6.86	10.15, 10.10	7.93, 7.91	4.57	8.85, 8.46	7.81, 7.68	${}^LH_o$ –0.90, ${}^LH_m$ 3.59, ${}^LCH_3$ 0.30, ${}^PCH_3$ –1.29, ${}^PCH_2$ –0.36
2-(4,4′-bipy)$_2$	6.92	10.18	8.00	4.60	8.84	7.82	Hα –0.64, Hβ 3.90, Hγ 5.51, Hδ 7.72
1-(4-MePy)	7.89	10.59, 7.35	8.09, 7.07	4.30	9.37	8.16	${}^LH_o$ –0.15, ${}^LH_m$ 4.09, ${}^LCH_3$ 0.61
1-(1-MeIm)	7.88	10.57, 7.37	8.09, 7.07	4.30	9.35	8.15	H_2 –0.38, H_4 0.89, H_5 3.82, CH_3 1.37
Ru(TPP′)(O)$_2$	9.11	8.26	7.36	4.14			
Fe(Pc)(4-MePy)$_2$					9.30	7.95	H_o 1.98, H_m 4.81, CH_3 1.07
Fe(Pc)[P(Me$_2$Ph)]$_2$					9.07	7.87	Hα 4.36, Hβ 6.24, Hγ 6.66, CH_3 –2.11
Fe(Pc)[P(OEt)$_3$]$_2$					9.26	7.91	CH_3 –0.20, CH_2 1.27
3-(1-MeIm)[a]	9.20	8.77	7.46	4.15	1.56 (DMG CH_3)		H_2 4.87, H_4 4.49, H_5 5.71, CH_3 2.83

[a] **3** = [Fe((DMG)BF$_2$)$_2$O]$_2$Ru(TPP′), ref. 6.

Fig. 5. Visible spectrum of **2** in $CHCl_3$. Insert shows the growth of the Pc Q band during the reductive cleavage of the oxo-bridge.

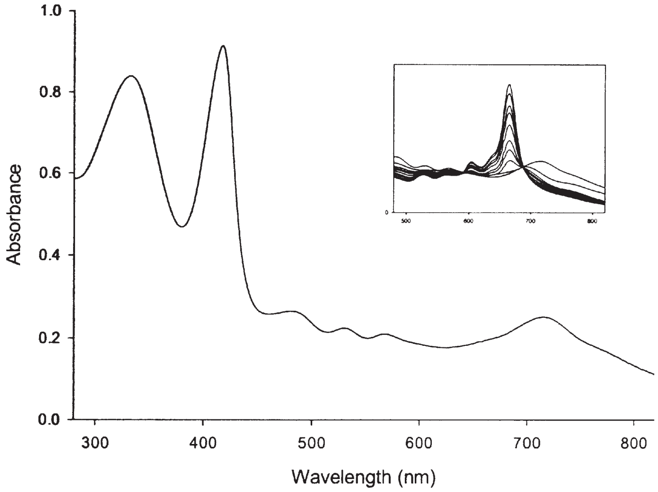
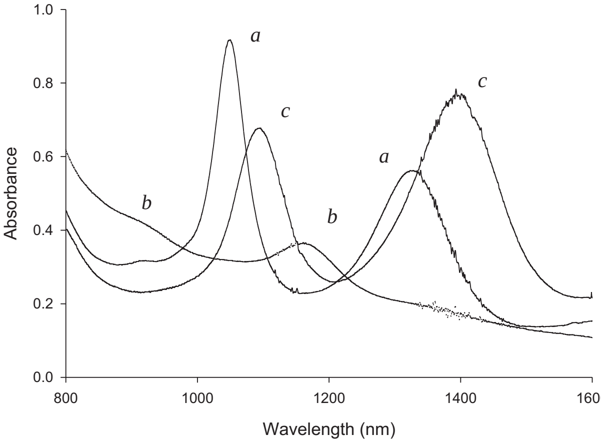


Fig. 6. Spectral changes in the near-IR region during the oxidation and subsequent reduction of **2**. (*a*) **2**-(4-MePy)$_2$; (*b*) [**2**-(4-MePy)$_2$]$^+$, obtained upon addition of 1 equiv. of [(η^5-Cp)$_2$Fe](PF$_6$); and (*c*) **2**-[(PMe$_2$Ph)]$_2$ obtained by addition of neat P(Me)$_2$Ph to the +1 ion.



Shifts in the near-IR as a function of axial ligand are similar to those previously described for Fe(DMG) systems (6).

Electrochemistry and redox reactions

Cyclic voltammetry experiments were carried out for **2** in CH_2Cl_2 containing 0.1 M (TBA)PF$_6$. Four reversible one-electron oxidation waves are observed for the 4-MePy adduct at –42°C and these occur at $E_{1/2}$ = 0.4, 0.76, 1.04, and 1.32 V (Fig. 7). The two lower oxidation waves are assigned to successive Fe$^{III/IV}$ oxidations in agreement with what previously reported for (PcFe)$_2$O (19). The third and fourth waves (1.04 and 1.32 V) are tentatively ascribed to successive oxidations of the Pc rings (20). Complex **2** shows a lower oxidation potential than the borylated dioxime-derived heterotrinuclear of Vernik (6) (Table 3).

The complex may be chemically oxidized to the +1 cation by using [(η^5-Cp)$_2$Fe](PF$_6$) ($E_{1/2}$ = 0.46 V in CH_2Cl_2). This chemical oxidation is reversible upon changing the axial ligand to P(CH$_3$)$_2$Ph. Figure 6 shows the change in the near-IR spectrum caused by the oxidation and subsequent reduction of the 4-MePy derivative. No reduction wave for **2** was detected up to –2.0 V. In related systems reduction normally results in irreversible oxo-bridge cleavage as electrons are added to antibonding orbitals (21).

Kinetics of reductive cleavage of oxo-bridge

The trinuclear complex undergoes slow reductive cleavage of the oxo-bridge with hydroquinones (H_2Q), phosphines, or phosphites. The kinetics of the reactions were studied at 40°C under anaerobic conditions and all changes were monitored by visible spectroscopy. Products were identified on the basis of distinctive visible–IR and ${}^1H$ NMR spectra and

Table 2. Visible and near-IR data for trinuclear $[(L)FeN_4O]_2Ru(TPP')$ oxo-bridged complexes (λ_{max}, nm).

N_4	Ligand	Soret	α	β	Q	CT1	CT2
Pc	4-MePy_2[a]	410	530	576	702	1050	1332
Pc	1-MeIm	410	528	566	702	1071	1325
Pc	$P(Me_2Ph)$	410	536	572	700	1096	1404
Pc	NH_3	412	526	572	702	1056	1312
Pc	CN^-	410	538	570	698	1130	1380
Pc	4,4′-bipy	412	532	572	702	1040	1340
Pc	pip	412	530	574	700	1088	1341
Pc	CH_3CN	410	530	568	702	1007	1300
$((DMG)BF_2)_2$[b]	1-MeIm	435	541	576		703	857
$((DMG)BPh_2)_2$[b]	1-MeIm	435	538	572		732	890
$((DPG)BF_2)_2$[b]	1-MeIm	433	542	577		714	836

[a] Extinction coefficient for $\mathbf{2}\text{-(4-MePy)}_2$ log (ε): 4.70, 4.18, 4.15, 4.33, 4.17, 4.03 for Soret, α, β, Q, CT1, and CT2, respectively. Other derivatives of **2** give comparable values.

[b] Ref. 6.

Table 3. Electrochemical data for trinuclear $[(L)FeN_4O]_2Ru(TPP')$ oxo-bridged complexes.

N_4	Ligand	$E_{1/2}$ (V)[a]	CT1	CT2
Pc	4-MePy	0.40, 0.76, 1.04, 1.32	1050	1332
$((DMG)BF_2)_2$[b]	CH_3CN	0.80, 1.20	691	812
$((DMG)BPh_2)_2$[b]	CH_3CN	0.60, 1.06	709	839
	NH_3	0.51, 1.04	716	850
$((DPG)BF_2)_2$[b]	CH_3CN	1.00	686	799

[a] Half-wave potentials for reversible oxidation.

[b] Ref. 6.

Table 4. Kinetic data for the reductive μ-oxo cleavage of trinuclear $[(L)FeN_4O]_2Ru(TPP')$ complexes.

N_4	Reductant	K_{obs} (1×10^{-4}) (s^{-1})
Pc[a]	$P(Me_2Ph)$	0.074
Pc[a]	$P(OEt)_3$	0.078
Pc[a]	H_2Q[b]	0.069
$((DMG)BF_2)_2$	H_2Q[c]	453
$((DPG)BF_2)_2$	H_2Q[c]	1340

[a] $[\mathbf{2}\text{-(4-MePy)}_2] = 1.0 \times 10^{-5}$ M. Reaction carried out in $CHCl_3$ at 40°C.

[b] In the presence of 4-MePy $(1.0 \times 10^{-3}$ M).

[c] Reaction carried out in CH_2Cl_2 at 25°C in the presence of 1 M CH_3CN. Ref. 6.

Fig. 7. Cyclovoltammogramm of **2** in CH_2Cl_2 at −42°C (Ag/Ag^+ used as the reference electrode).

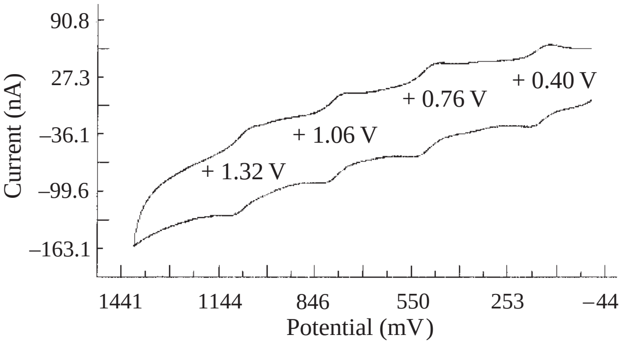
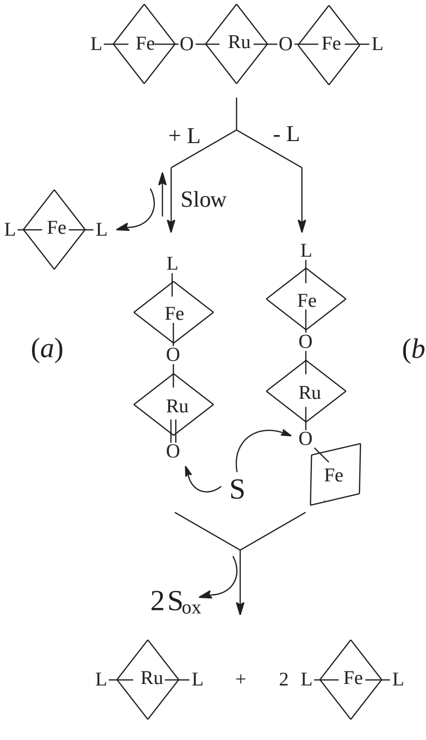


Fig. 8. Possible pathways of oxo-bridge reductive cleavage in trinuclear complexes. (*a*) Dissociative path; occurs in $[(L)Fe(N_4)O]_2Ru(TPP')$ complexes where N_4 is the Pc ring. The rate-determining step is the dissociation of a Fe(Pc) unit. (*b*) Bent μ-oxo path; occurs in $[(L)Fe(N_4)O]_2Ru(TPP')$ complexes where N_4 is the DMG or the DPG ring. The rate-determining step involves oxo-transfer from the trinuclear to S; S = reducing substrate (H_2Q, $P(Me_2Ph)$, or $P(OEt)_3$).



the overall stoichiometry shown in eqs. [2] and [3] was confirmed by NMR.

$$[2] \quad \mathbf{2}\text{-(4-MePy)}_2 + 8PX_3 \rightarrow 2Fe(Pc)(PX_3)_2 + Ru(TPP')(PX_3)_2 + 2(O{=}PX_3)$$

$$[3]\qquad \mathbf{2}\text{-}(\mathrm{L})_2 + 4\mathrm{L} + 2\mathrm{H_2Q} \rightarrow 2\mathrm{Fe(Pc)(L)_2} + \mathrm{Ru(TPP')(L)_2} + 2\mathrm{Q}\ (\text{where L} = \text{4-MePy})$$

The rate constant for the reduction of **2** ($7 \times 10^{-6}\ \mathrm{s}^{-1}$) was found to be independent of the concentration or nature of the reductant used and it is at least four orders of magnitude slower than that of μ-oxo borylated dioxime systems (6) (see Table 4). The reaction proceeds cleanly (isosbestic point at 688 nm) with no binuclear or other intermediates detected. Mechanism A in Fig. 8 is proposed in which the rate determining step is the dissociation of a Fe(Pc) unit to generate a binuclear species, which is subsequently reduced to the monomeric $\mathrm{Ru^{II}(TPP')}$ and $\mathrm{Fe^{II}(Pc)}$ complexes. In contrast, mechanism B was proposed in DMG systems where reduction was found to show an inverse first-order dependence on the axial ligand concentration implying a loss of one ligand prior to the rate determining μ-oxo cleavage (6, 22). A folding back of the pentacoordinate $\mathrm{FeN_4}$ fragment in a bent geometry permits direct attack at the oxo site in these systems. Mechanism B may be much more difficult in FePc-based trinuclears as the Pc ring lacks the flexibility of the DMG macrocycles. Thus, only a [L] independent dissociative path is observed in the FePc systems.

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References

1. (*a*) R.D. Holm. Chem. Rev. **87**, 1401 (1987); (*b*) D.M. Kurtz. Chem. Rev. **90**, 585 (1990); (*c*) R.D. Holm, P. Kennepohl, and E.I. Solomon. Chem. Rev. **96**, 2239 (1996); (*d*) B.J. Waller and J.D. Lipson. Chem. Rev. **96**, 2625 (1996); (*e*) P. Norlund, B.-M. Sjöberg, and H. Eklund. Nature (London), **345**, 593 (1990); (*g*) R.M. Buchanan, S. Chen, and J.F. Richardson. Inorg. Chem. **33**, 3208 (1994); (*h*) K. Neimann, R. Neumann, and A. Ribion. Inorg. Chem. **38**, 3575 (1999).
2. C. Ercolani and B. Floris. *In* Phthalocyanines. Properties and applications. Vol. 2. *Edited by* C.C. Leznoff and A.B.P. Lever. VCH Publishers, New York. 1993. pp. 1–42.
3. (*a*) R.D. Cannon and R.P. White. Prog. Inorg. Chem. **36**, 195 (1988); (*b*) M.H. Chisholm, K. Folting, and E.M. Kober. Inorg. Chem. **24**, 241 (1985).
4. (*a*) E.N. Baski, R.L. Elliott, K.S. Murray, P.J. Nichols, and B.O. West. Aust. J. Chem. **43**, 707 (1990); (*b*) B.O. West. Polyhedron, **8**, 219 (1989); (*c*) D.J. Liston, B.J. Kennedy, K.S. Murray, and B.O. West. Inorg. Chem. **24**, 1561 (1985); (*d*) R.J. Saxton, L.W. Olson, and L.J.J. Wilson. J. Chem. Soc. Chem. Commun. 984 (1982).
5. (*a*) A. Yamamoto, L.K. Phillips, and M. Calvin. Inorg. Chem. **7**, 847 (1968); (*b*) A.B.P. Lever, J.P. Wilshire, and K.S. Quan. Inorg. Chem. **20**, 761 (1981); (*c*) C. Ercolani, M. Gardini, F. Monacelli, G. Pennesi, and G. Rossi. Inorg. Chem. **22**, 2584 (1983); (*d*) C. Ercolani, G. Rossi, and F. Monacelli. Inorg. Chem. Acta, **44**, L215 (1980).
6. I. Vernik and D.V. Stynes. Inorg. Chem. **37**, 10 (1998).
7. (*a*) K.J. Berry, B. Moubaraki, K.S. Murray, P.J. Nichols, L.D. Schultz, and B.O. West. Inorg. Chem. **34**, 4123 (1995); (*b*) L.D. Schultz, G.D. Fallon, B. Moubaraki, K.S. Murray, and B.O. West. J. Chem. Soc. Chem. Commun. 971 (1992).
8. A.D. Alder, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, and L. Koskakoff. J. Org. Chem. **32**, 476 (1967).
9. J.P. Collman, C.E. Barnes, P.J. Brothers, T.J. Collins, T. Ozawa, J.C. Gallucci, and J.A. Ibers. J. Am. Chem. Soc. **106**, 5151 (1984).
10. W. Leung and C.M. Che. J. Am. Chem. Soc. **111**, 8812 (1989).
11. D.V. Stynes and B.R. James. J. Am. Chem. Soc. **96**, 2733 (1974).
12. (*a*) R.J. Abraham, S.C.M. Fell, and K.M. Smith. Org. Magn. Reson. **9**, 367 (1977); (*b*) R.J. Abraham, G.R. Bedford, D. McNeillie, and B. Wright. Org. Magn. Reson. **14**, 418 (1980); (*c*) R.J. Abraham, G.R. Bedford, B. Wright. Org. Magn. Reson. **18**, 45 (1982); (*d*) R.J. Abraham, C.J. Medforth, K.M. Smith, D.A. Goff, and D.J. Simpson. J. Am. Chem. Soc. **109**, 4786 (1987).
13. C. Ercolani, J. Jubb, G. Pennesi, U. Russo, and G. Trigante. Inorg. Chem. **34**, 2535 (1995).
14. K.J. Wynne. Inorg. Chem. **24**, 1339 (1985).
15. M.T. Pinillos, A. Elduque, E. Martin, N. Navarro, J.F. Lahoz, J.A. Lopez, and L. Oro. Inorg. Chem. **34**, 111 (1995).
16. B.J. Hamstra, B. Cheng, and M.K. Ellison. Inorg. Chem. **38**, 3554 (1999).
17. M.P. Donzello, C. Ercolani, K.M. Kadish, Z. Ou, and U. Russo. Inorg. Chem. **37**, 3682 (1998).
18. D.J. Liston, B.J. Kennedy, K.S. Murray, and B.O. West. Inorg. Chem. **24**, 1567 (1985).
19. L.A. Bottomley, C. Ercolani, J.-N. Gorce, G. Pennesi, and G. Rossi. Inorg. Chem. **25**, 2338 (1986).
20. (*a*) M. Hannak, A. Lange, M. Rein, R. Behnisch, G. Renz, and A. Leverenz. Synth. Metal, **29**, F1 (1989); (*b*) R. Behnisch and M. Hannak. Synth. Metal, **36**, 387 (1990); (*c*) W. Kalz, H. Homborg, H. Kuppers, B.J. Kennedy, and K.S. Murray. Naturforsch. **B39b**, 1478 (1984); (*d*) Y. Orihashi, H. Ohno, E. Tsuchida, H. Matsuda, H. Nakanishi, and M. Kato. Chem. Lett. 601 (1987); (*e*) Y. Orihashi, N. Nishikawa, H. Ohno, E. Tsuchida, H. Matsuda, H. Nakanishi, and M. Kato. Bull. Chem. Soc. Jpn. **60**, 3731 (1987).
21. (*a*) M. Muller, B. Eckhard, T. Weyhermuller, and K. Wieghardt. Chem. Commun. 705 (1997); (*b*) J.D. Cohen, S. Payne, K.S. Hagen, and J. Sanders-Loehr. J. Am. Chem. Soc. **119**, 2960 (1997); (*c*) U. Bossek, H. Hummel, T. Weyhermuller, E. Bill, and K. Wieghardt. Angew. Chem. Int. Ed. Engl. **34**, 2642 (1995); (*d*) D.V. Stynes, H. Noglik, and D.W. Thompson. Inorg. Chem. **30**, 4567 (1991); (*e*) J.E. Early and T. Fealey. Inorg. Chem. **25**, 2015 (1986).
22. (*a*) I. Vernik and D.V. Stynes. Inorg. Chem. **35**, 2006 (1996); (*b*) J.M. Caroll and J.R. Norton. J. Am. Chem. Soc. **114**, 8744 (1992).