Formation of heterobinuclear μ-nitrido complexes with a Mn–N–Fe moiety by reaction of nitrido(octaphenyltetraazaporphyrinato)manganese(V) with iron(III) porphyrins

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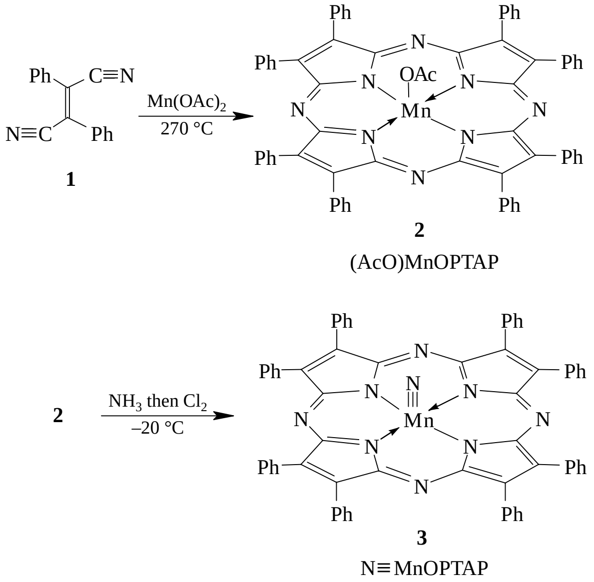
Nitrido(octaphenyltetraazaporphyrinato)manganese(V) (N≡MnOPTAP) obtained by treatment of chlorine on acido(octaphenyltetraazaporphyrinato)manganese(III) [(X)MnOPTAP; X = Cl, AcO, HSO_4] in chloroform solution saturated with ammonia, reacts with acido(octaphenyltetraazaporphyrinato)iron(III) [(X)FeOPTAP; X = Cl, Br, AcO] forming the heterometallic μ-nitrido complex μ-(MnNFe)$(OPTAP)_2$; μ-nitrido complexes with a dissimilar porphyrin ligand on each metal have also been prepared.

Binuclear μ-nitrido iron complexes of porphyrins,[1] tetraazaporphyrins[2] and phthalocyanine[3,4] can be easily obtained by thermolysis of the corresponding azidoiron(III) complexes. Heating of azido(tetraphenylporphyrinato)iron(III) [(N_3)FeTPP] in the presence of iron or ruthenium phthalocyanines (FePc, RuPc) results in the formation of mixed binuclear μ-nitrido complexes (TPP)Fe(μ-N)Fe(Pc) and (TPP)Fe(μ-N)Ru(Pc).[5] It was supposed[1,6] that nitrido(tetraphenylporphyrinato)iron(V) (N≡FeTPP) is a reactive intermediate in the formation of μ-N$(FeTPP)_2$ from (N_3)FeTPP. However, due to the extremely high instability of the nitridoiron(V) complexes [N≡FeTPP was detected[7] as a photolysis product of (N_3)FeTPP only below 150 K] their role in μ-nitrido complex formation has not received any direct confirmation as yet. Unlike nitridoiron(V) complexes nitridomanganese(V) complexes of porphyrins[8] and phthalocyanines[9] are very stable. In order to throw some light on the mechanism of the μ-nitrido complex formation, we have obtained stable nitrido(octaphenyltetraazaporphyrinato)manganese(V) (N≡MnOPTAP **3**; Scheme 1) and attempted to use it in the synthesis of the heterometallic μ-nitrido complexes (Scheme 2).



1

2 (AcO)MnOPTAP

3 N≡MnOPTAP

Scheme 1

Melting of (*E*)-1,2-diphenyl-1,2-dicyanoethylene **1** with anhydrous manganese(II) acetate in a 1:1 molar ratio at 270 °C gave acetato(octaphenyltetraazaporphyrinato)manganese(III) [(AcO)MnOPTAP **2**; yield 85%].[†] N≡MnOPTAP **3** was obtained by bubbling chlorine through a cooled (–20 °C) solution of **2** in chloroform saturated with gaseous ammonia (yield 61%).[‡] Other acidomanganese(III) complexes (X)MnOPTAP (*e.g.* X = Cl, HSO_4) can also be used as a starting material. Complex **2** can bind ammonia as an axial ligand forming hexacoordinated ammine complexes of manganese(III), (AcO)(H_3N)MnOPTAP, or on more prolonged exposition of manganese(II), $(H_3N)_2$MnOPTAP. Coordination of ammonia to **2** and subsequent conversion of the ammine complexes to N≡MnOPTAP under action of chlorine can be followed by UV/VIS spectroscopy (Figure 1). Whereas the spectrum of (AcO)(H_3N)MnOPTAP is almost identical with that of **2** [Figure 1(*a*)], additional characteristic bands appear at 830 and 886 nm for $(H_3N)_2$MnOPTAP [Figure 1(*b*)]. These ammine complexes can be chlorinated to give, we suppose, unstable intermediate complexes containing *N*,*N*-dichloroamidomanganese(III), (Cl_2N)MnOPTAP, or *N*-chloronitrenomanganese(IV), ClN=MnOPTAP, which easily split off chlorine forming stable nitridomanganese(V) complex **3** [Figure 1(*c*)]. In the absence of ammonia complex **2** is oxidized irreversibly with chlorine producing colourless products. A substantial hypsochromical shift of the $\pi \rightarrow \pi^*$ transitions of the macrocycle observed for **3** as compared with **2** is in agreement with strengthening of the π-donation effect expected for d^2 complexes such as N≡MnOPTAP.

The structure of **3** is confirmed by the presence in the mass spectrum of a molecular ion peak of N≡MnOPTAP$^+$ at $m/z = 990.4$ and by the appearance of the Mn≡N stretching vibration as a weak band at 1054 cm^{-1} in the IR spectrum and as a medium-strong line at 1058 cm^{-1} in the resonance Raman spectrum.

The heterometallic μ-nitrido complex **5**, μ-(MnNFe)-$(OPTAP)_2$, was obtained by reaction of the nitridomanganese(V) complex **3** with chloroiron(III) complex **4**, (Cl)FeOPTAP,[10] in a boiling benzene solution (**3**:**4** = 1:1.5 molar ratio) (Scheme 2). The μ-nitrido complex **5** was chromatographically purified and separated from an admixture of μ-oxodimer O$(FeOPTAP)_2$, formed partially from **4** (neutral Al_2O_3, eluent $CHCl_3$, yield of **5** 23%).[§] The Mn/Fe ratio determined by a flame photometry

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[†] *Spectral data* for **2**: Found (%): C, 76.28; H, 4.54; N, 10.49. Calc. for $C_{66}H_{43}N_8O_2Mn$ (%): C, 76.59; H, 4.19; N, 10.83. UV/VIS [$CHCl_3$, λ_{max}/nm (log ε)]: 285 (4.66), 331sh, 414 (4.56), 475 (4.39), 613sh, 665 (4.60). Camenzind and Hill[11] have reported the preparation of octaphenyltetraazaporphyrinatomanganese(II) from **1** and manganese powder with low yield (5.7%); no spectral data have been reported for this compound.

[‡] *Spectral data* for **3**: Found (%): C, 77.76; H, 4.18; N, 12.55. Calc. for $C_{64}H_{40}N_9Mn$ (%): C, 77.65; H, 4.07; N, 12.73. FD-MS *m*/*z*: N≡MnOPTAP$^+$ (990.4, 12%); MnOPTAP$^+$ (975.3, 100%). UV/VIS [$CHCl_3$, λ_{max}/nm (log ε)]: 270sh, 345sh, 361 (4.65), 447 (4.22), 577 (4.12), 601sh, 629 (4.91).

[§] *Spectral data* for **5**: Found (%): C, 77.84; H, 3.95; N, 12.03; Mn, 2.72; Fe, 2.6. Calc. for $C_{128}H_{80}N_{17}MnFe$ (%): C, 78,16; H, 4.10; N, 12.11; Mn, 2.79; Fe, 2.84. FD-MS *m*/*z*: N≡MnOPTAP$^+$ (990.4, 2.9%), FeOPTAP$^+$ (976.3, 89%), MnOPTAP$^+$ (975.3, 100%). UV/VIS [$CHCl_3$, λ_{max}/nm (log ε)]: 345 (4.81), 437sh, 583 (4.55), 642 (4.66).

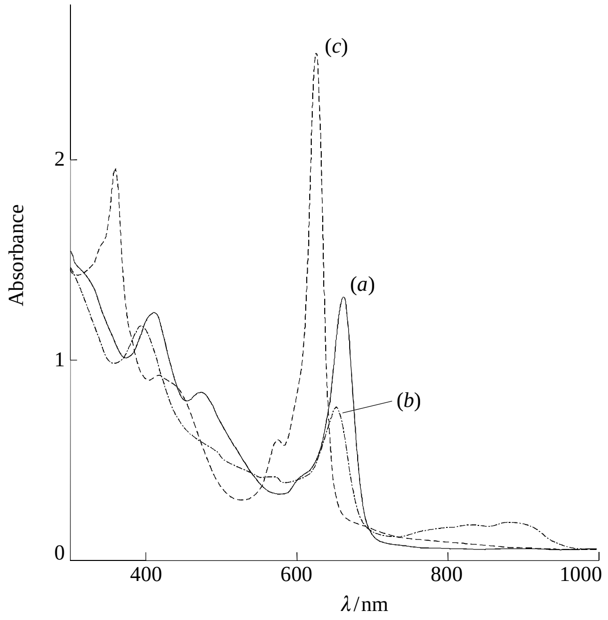


Figure 1 UV/VIS spectra of (*a*) (AcO)MnOPTAP in chloroform (3.5×10^{-5} M); (*b*) after saturation with ammonia at –20 °C; (*c*) after bubbling of chlorine.

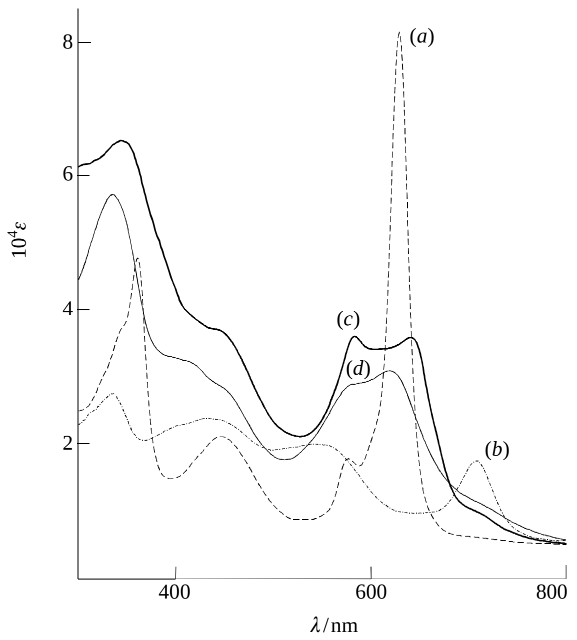
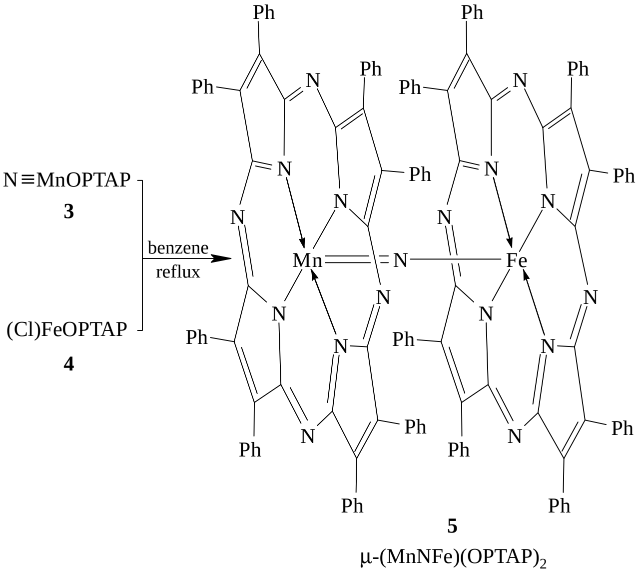


Figure 2 UV/VIS spectra of (*a*) N≡MnOPTAP; (*b*) (Cl)FeOPTAP; (*c*) μ-(MnNFe)(OPTAP)$_2$ and (*d*) μ-N(FeOPTAP)$_2$ in chloroform.

method and the CHN elemental analysis data for **5** are in reasonable agreement with the proposed formula, μ-(MnNFe)(OPTAP)$_2$. The mass spectrum of **5** obtained by a field desorption method contains mass peaks (in m/z) corresponding to the monomer constituents of the mixed μ-nitrido complex (N≡MnOPTAP$^+$ 990.4; MnOPTAP$^+$ 975.3; FeOPTAP$^+$ 976.3), but no molecular ion peak expected for $C_{128}H_{80}N_{17}MnFe$ at m/z = 1965.6 has been detected.

Formation of **5** can be easily monitored by UV/VIS spectroscopy: characteristic absorption bands of the initial complexes **3** (629 nm) and **4** (710 nm) disappear and a broad doublet (642, 583 nm) appears. Such splitting of the Q-band, being a result of excitonic interactions of the adjacent π-systems, is characteristic of binuclear single atom bridged complexes. The UV/VIS spectrum of the mixed Mn–Fe μ-nitrido complex **5** [μ-(MnNFe)(OPTAP)$_2$, Figure 2(*c*)] is similar to the spectrum of the homobinuclear μ-nitridodiiron complex [μ-N(FeOPTAP)$_2$, Figure 2(*d*)], but the maxima of the Q-band envelope are bathochromically shifted. No metal-axial ligand stretching vibrations characteristic of the initial complexes **3** and **4** ($\nu_{Mn\equiv N}$ = 1054 cm^{-1} for **3** and ν_{Fe-Cl} = 310 cm^{-1} for **4**) are present in the IR spectrum of **5** and a medium-weak band at 918 cm^{-1} appears likely to be associated with the MnNFe bridge (FeNFe absorbs at 920 cm^{-1}). The dinuclear identity of **5** has also been confirmed by its reaction with acids HX (HX = HCl, H_2SO_4, AcOH, CCl_3COOH) which causes decomposition to the mononuclear complexes of Mn and Fe [(X)MnOPTAP and/or N≡MnOPTAP and (X)FeOPTAP], each of which can be separated by thin-layer chromatography and identified by UV/VIS spectroscopy. It has been verified that reaction of N≡MnOPTAP with bromoiron(III), acetatoiron(III) and μ-oxodiiron(III) derivatives of octaphenyltetraazaporphine [(Br)FeOPTAP, (AcO)FeOPTAP and μ-O(FeOPTAP)$_2$] also leads to **5**. Mixed Mn–Fe μ-nitrido species containing dissimilar macrocyclic ligands bound to each metal can be obtained by coupling of the corresponding nitridomanganese(V) and iron(III) complexes, thus reaction of N≡MnOPTAP with (AcO)FeTPP gives (OPTAP)Mn(μ-N)Fe(TPP).



5
μ-(MnNFe)(OPTAP)$_2$

Scheme 2

Whether the μ-(MnNFe) bridge has an asymmetrical bond distribution (Mn^{III}–N=Fe^{IV} or Mn^{IV}=N–Fe^{III} as shown in Scheme 2) or its structure is more symmetrical (Mn┄N┄Fe) similar to the (Fe┄N┄Fe) bridge in μ-N(FeOPTAP)$_2$[2] is not yet clear. Physicochemical properties of mixed Mn–Fe μ-nitrido complexes of porphyrins as well as details of the mechanism of their formation are presently under investigation.

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