EPR SPECTRA OF PENTA- OR HEXACOORDINATE NITROSYL HEMES WITH STERICALLY MODIFIED PORPHYRIN CORES

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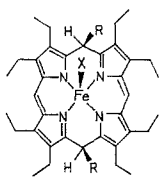

Fe(OEPR$_2$)X; X=NO

2a: R = Me
Me = CH_3
3a: R = CMe_3

Nitrosyliron(II)porphyrins show a tendency to exist as pentacoordinate species, e.g., the octaethylporphyrin derivative, Fe(OEP)NO (1a) [1], and the porphodimethene derivative Fe(OEPMe$_2$)NO (2a) [2] have been described. The rooflike folding of the porphodimethene core does not seem to have a large effect on the EPR spectrum [3]; both 1a and 2a add pyridine(Py)trans to NO when the toluene solution contains Py. Replacement of the methyl groups in 2a by t-butyl groups allows the formation of 3a which does not add Py as its spectrum remains unaltered in the presence of Py. This is due to direct or indirect sterical hindrance by the t-butyl groups.

TABLE: EPR parameters [3] of various nitrosyl hemes 1-3 (in frozen toluene (a) or Py/toluene (b; 1:9), T = 77K, Bruker B-ER 420, X-band; a: hyperfine coupling constant [mT])

Compound		No.	g_{xx}	g_{yy}	g_{zz}	a(^{14}NO)	a(^{14}NPy)
Fe(OEP)NO	(a)		2.107	2.061	2.010	1.68	
Fe(OEP)NO·Py	(b)		2.083	1.980	2.003	2.21	0.68
Fe(OEPMe$_2$)NO	(a)	2a	2.091	2.027	2.009	1.61	
Fe(OEPMe$_2$)NO·Py	(b)	2b	2.082	1.974	2.005	2.12	0.706
Fe(OEPBut$_2$)NO	(a,b)	3a	2.091	2.058	2.011	1.65	

[1] R. Bonnett, A.A. Charalambidis, R.A. Martin, K.D. Sales and B.W. Fitzsimmons, J.C.S.Chem. Commun. 1975, 884.
[2] J.W. Buchler and K.L. Lay, Z.Naturforsch. 30b, 385 (1975).
[3] J. Billecke, Dissertation, Technische Hochschule Aachen, 1980.