Six Non-equivalent Nitrogen Atoms in Octahedral *mer*-[Fe(fbpy)$_3$]$^{2+}$ (fbpy = 4-fluoro-2,2′-bipyridine)

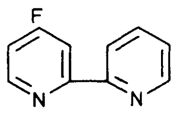
A. F. Janzen,* T. Q. Nguyen, Fanqi Qu, and K. Marat

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

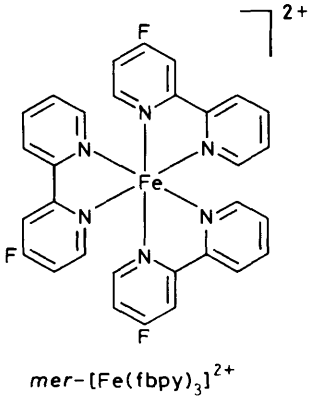
The ^{15}N n.m.r. spectra of fbpy (4-fluoro-2,2′-bipyridine), [Fe(bpy)$_3$]$^{2+}$, *cis*-[Co(bpy)$_2$(H$_2$O)$_2$]$^{3+}$, and a 3 : 1 mixture of *mer*- and *fac*-[Fe(fbpy)$_3$]$^{2+}$, are reported; in the case of *mer*-[Fe(fbpy)$_3$]$^{2+}$, the lack of symmetry makes all six nitrogen atoms non-equivalent and this non-equivalence is confirmed by ^{15}N n.m.r. spectroscopy.

Fay and Piper[1] found that a mixture of *mer*- and *fac*-isomers of a metal trifluoroacetylacetonate, M(tfac)$_3$, gave four CF$_3$ signals in the ^{19}F n.m.r. spectrum, three from the *mer*- and one from the *fac*-isomer. As part of our studies of fluorine exchange in various trigonal bipyramidal and octahedral compounds,[2] we synthesized 4-fluoro-2,2′-bipyridine (fbpy) and prepared a series of octahedral complexes containing the fbpy or bpy (2,2′-bipyridine) ligand. A statistical 3 : 1 mixture of *mer*- and *fac*-[Fe(fbpy)$_3$]$^{2+}$ showed[3] four signals of equal intensity in the ^{19}F n.m.r. spectrum at −97.69, −97.72, −97.78, and −97.82 p.p.m., three assigned to *mer*-[Fe(fbpy)$_3$]$^{2+}$ and one to *fac*-[Fe(fbpy)$_3$]$^{2+}$, but these isomers have not, so far, been separated. *mer*-[Fe(fbpy)$_3$]$^{2+}$ is of particular interest because its lack of symmetry makes all six nitrogen atoms in the octahedral inner co-ordination sphere non-eqivalent; we therefore examined the ^{15}N n.m.r. spectrum to see if this non-equivalence could be observed.

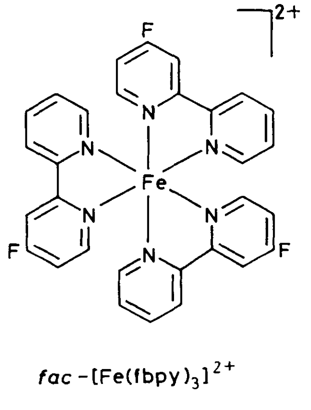
The ^{15}N n.m.r. spectra of several bpy and fbpy complexes are shown in Figure 1. As expected, [Fe(bpy)$_3$]$^{2+}$ gives a single peak [Figure 1(a)], and *cis*-[Co(bpy)$_2$(H$_2$O)$_2$]$^{3+}$ gives two singlet peaks [Figure 1(b)], while the non-equivalent nitrogen atoms of fbpy [Figure 1(c)] give rise to a singlet ('pyridyl') and



fbpy



mer-[Fe(fbpy)$_3$]$^{2+}$



fac-[Fe(fbpy)$_3$]$^{2+}$

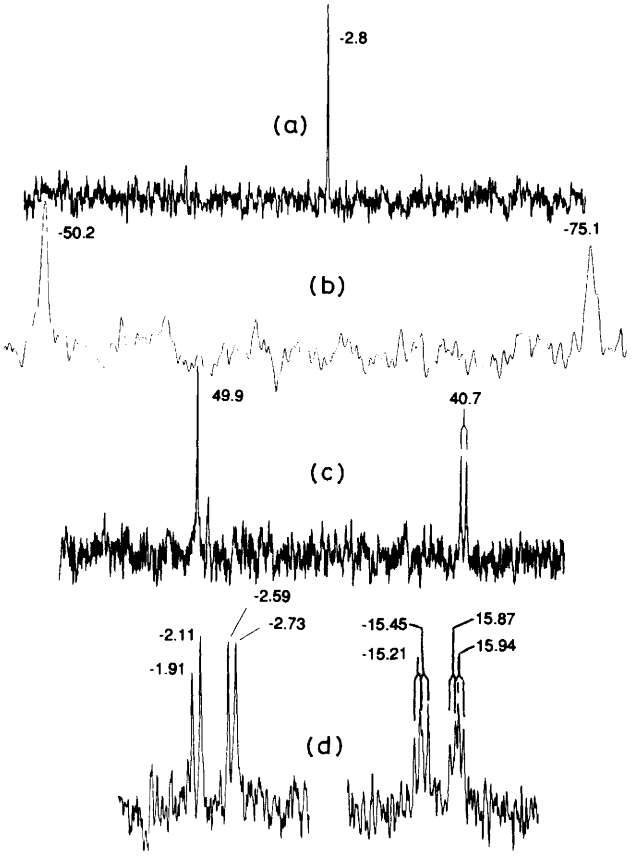


Figure 1. Natural abundance, proton-decoupled, ^{15}N n.m.r. spectra recorded with a Bruker AM300 spectrometer at 30.4 MHz: (a) $[Fe(bpy)_3]Cl_2$ in D_2O; (b) *cis*-$[Co(bpy)_2(H_2O)_2](PF_6)_3$ in D_2O; (c) fbpy in $CDCl_3$; (d) 3:1 mixture of *mer*- and *fac*-$[Fe(fbpy)_3](PF_6)_2$ in $(CD_3)_2CO$. Chemical shifts were measured relative to an external sample of pyridine in $(CD_3)_2CO$ and converted to the nitromethane scale by addition of 61.79 p.p.m.[5]

a doublet ('fluoropyridyl') peak, with $^4J(FN)$ 6 Hz. Figure 1(d) shows the spectrum of a 3:1 mixture of *mer*- and *fac*-$[Fe(fbpy)_3]^{2+}$. From symmetry considerations, three singlets ('pyridyl') and three doublets ('fluoropyridyl') are expected for the six non-equivalent nitrogens in *mer*-$[Fe(fbpy)_3]^{2+}$, and one singlet and one doublet for the two sets of non-equivalent nitrogen atoms in *fac*-$[Fe(fbpy)_3]^{2+}$; Figure 1(d) confirms the presence of a total of four singlet and four doublet nitrogen peaks, of approximately equal intensity. These results demonstrate that each of the six non-equivalent nitrogen atoms in *mer*-$[Fe(fbpy)_3]^{2+}$ can be observed by ^{15}N n.m.r. spectroscopy. In view of the continuing interest in transition metal–bipyridyl systems,[4] the fbpy ligand, combined with ^{15}N and ^{19}F n.m.r. spectroscopy, may be useful in further stereochemical and mechanistic studies of these systems.

We thank N.S.E.R.C. of Canada and the University of Manitoba Research Committee for financial support.

Received, 19th April 1988; Com. 8/01504J

References

1 R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, 1963, **85**, 500.
2 R. K. Marat and A. F. Janzen, *Can. J. Chem.*, 1977, **55**, 3845; *Inorg. Chem.*, 1980, **19**, 798; A. S. Secco, K. Alam, B. J. Blackburn, and A. F. Janzen, *Inorg. Chem.*, 1986, **25**, 2125.
3 X. Huang, T. Q. Nguyen, and A. F. Janzen, 8th Winter Fluorine Conference, St. Petersburg, Florida, Jan. 25—30, 1987.
4 D. W. Pipes and T. J. Meyer, *Inorg. Chem.*, 1986, **25**, 4042; M. H. Chisholm, J. A. Connor, J. C. Huffman, E. M. Kober, and C. Overton, *ibid.*, 1984, **23**, 2298, and references cited therein.
5 H. J. Jakobsen, P. I. Yang, and W. S. Brey, *Org. Magn. Reson.*, 1981, **17**, 290.