The dataset contains:

Analytical characterisation of the complexes (CHN microanalysis)

X-ray Crystallographic data:

- Structure of [Fe((*S*)-*L*^{1}Ph)((*R*)-*L*^{2}Ph)][ClO_4]$_2$·$MeNO_2$ (**1**·$MeNO_2$; CCDC 2132824)
- Structure of [Fe((*R*)-*L*^{1}*i*Pr)((*S*)-*L*^{2}*i*Pr)][ClO_4]·MeCN (**2**·MeCN; CCDC 2132825)
- Structure of [Fe((*R*)-*L*^{1}Ph)(bimpy)][ClO_4]$_2$·MeCN (**3**·MeCN; CCDC 2132826)
- Structure of [Fe((*R*)-*L*^{2}Ph)(bimpy)][ClO_4]$_2$ (**4**; CCDC 2132827)
- Structure of [Fe((*S*)-*L*^{1}*i*Pr)(bimpy)][ClO_4]$_2$ (**5**; CCDC 2132828)
- Structure of [Fe((*S*)-*L*^{2}*i*Pr)(bimpy)][ClO_4]$_2$·MeCN·Et_2O (**6**·MeCN·Et_2O; CCDC 2132829)
- Structure of [Fe((*R*)-*L*^{2}Ph)(bpp)][ClO_4]$_2$·2MeCN (**8**·2MeCN; CCDC 2132830)
- Structure of [Fe(terpy)$_2$][ClO_4]$_2$·2MeCN (CCDC 2134550).

X-ray powder diffraction data (measured and simulated).

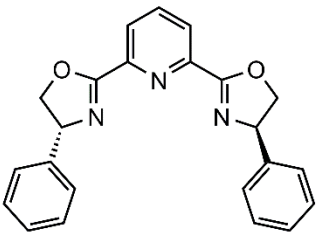
^{1}H NMR spectra (raw data and plotted spectra).

Solid state magnetic susceptibility measurements (raw and processed data).

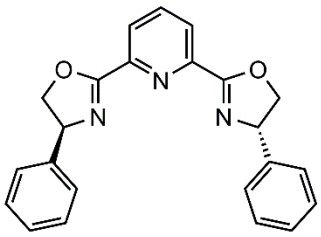
Solution magnetic susceptibility measurements (raw spectra and calculated χ_MT values).

DFT calculations (*SPARTAN* files).

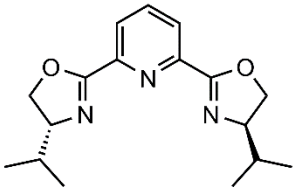
Ligands referred to in this study



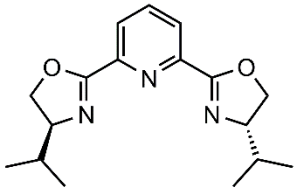
2,6-*Bis*(4-(*R*)-phenyl-4,5-dihydrooxazol-2-yl)pyridine
$C_{23}H_{19}N_3O_2$
(*R*)-*L*^{1}Ph



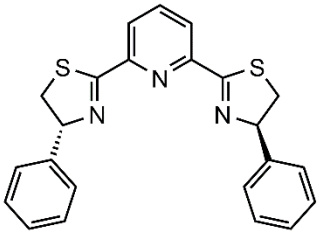
2,6-*Bis*(4-(*S*)-phenyl-4,5-dihydrooxazol-2-yl)pyridine
$C_{23}H_{19}N_3O_2$
(*S*)-*L*^{1}Ph



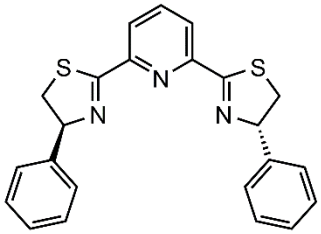
2,6-Bis(4-(R)-isopropyl-4,5-dihydrooxazol-2-yl)pyridine
$C_{17}H_{23}N_3O_2$
(R)-*L*^{1}*i*Pr



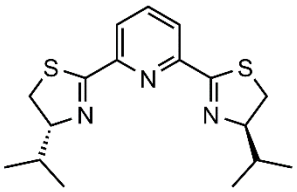
2,6-*Bis*(4-(*S*)-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridine
$C_{17}H_{23}N_3O_2$
(*S*)-*L*^{1}*i*Pr



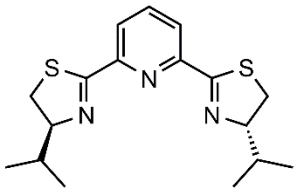
2,6-*Bis*(4-(*R*)-phenyl-4,5-dihydrothiazol-2-yl)pyridine
$C_{23}H_{19}N_3S_2$
(*R*)-*L*^{2}Ph



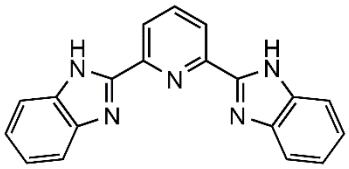
2,6-*Bis*(4-(*S*)-phenyl-4,5-dihydrothiazol-2-yl)pyridine
$C_{23}H_{19}N_3S_2$
(*S*)-*L*^{2}Ph



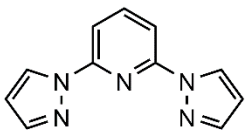
2,6-Bis(4-(*R*)-isopropyl-4,5-dihydrothiazol-2-yl)pyridine
$C_{17}H_{23}N_3S_2$
(R)-*L*^{2}*i*Pr



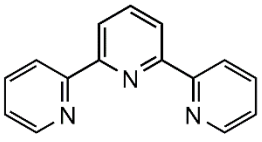
2,6-*Bis*(4-(*S*)-*iso*propyl-4,5-dihydrothiazol-2-yl)pyridine
$C_{17}H_{23}N_3S_2$
(*S*)-*L*^{2}*i*Pr



2,6-*Bis*(benzimidazol-2-yl)pyridine
$C_{19}H_{13}N_5$
bimpy

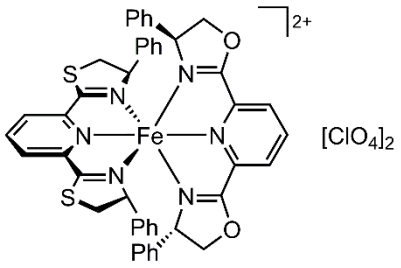


2,6-*Bis*(pyrazol-1-yl)pyridine
$C_{11}H_9N_5$
bpp



2,2':6',2''-Terpyridine
$C_{15}H_{11}N_3$
terpy

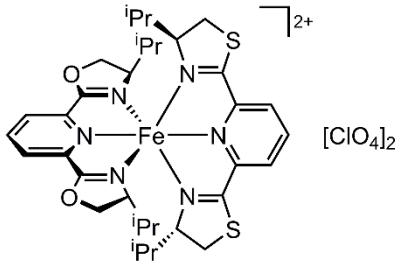
Complexes referred to in this study



[2,6-*Bis*((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)pyridine]-[2,6-*bis*((*R*)-4-phenyl-4,5-dihydrothiazol-2-yl)pyridine]-iron(II) diperchlorate

$C_{46}H_{38}Cl_2FeN_6O_{10}S_2$

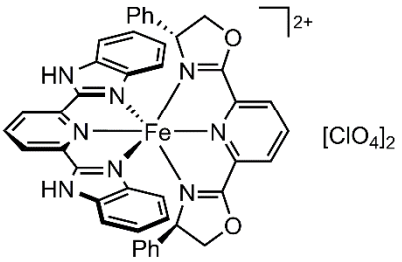
[Fe((*S*)-L^1Ph)((*R*)-L^2Ph)][ClO_4]$_2$ (**1**)



[2,6-*Bis*((*R*)-4-*iso*propyl4,5-dihydrooxazol-2-yl)pyridine]-[2,6-*bis*((*S*)-4-*iso*propyl-4,5-dihydrothiazol-2-yl)pyridine]-iron(II) diperchlorate

$C_{34}H_{46}Cl_2FeN_6O_{10}S_2$

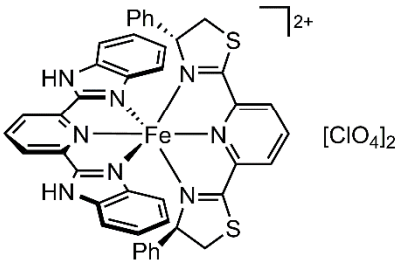
[Fe((*R*)-L^1*i*Pr)((*S*)-L^2*i*Pr)][ClO_4]$_2$ (**2**)



[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrooxazol-2-yl)pyridine]-[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II) diperchlorate

$C_{42}H_{32}Cl_2FeN_8O_{10}$

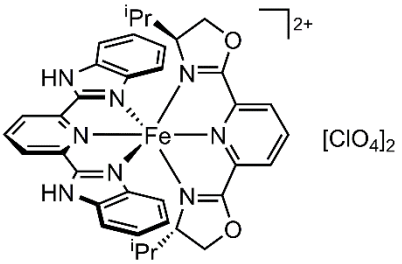
[Fe((*R*)-L^1Ph)(bimpy)][ClO_4]$_2$ (**3**)



[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrothiazol-2-yl)pyridine]-[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II) diperchlorate

$C_{42}H_{32}Cl_2FeN_8O_8S_2$

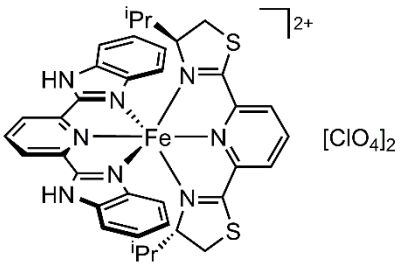
[Fe((*R*)-L^2Ph)(bimpy)][ClO_4]$_2$ (**4**)



[2,6-*Bis*((*S*)-4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridine]-[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II) diperchlorate

$C_{36}H_{36}Cl_2FeN_8O_{10}$

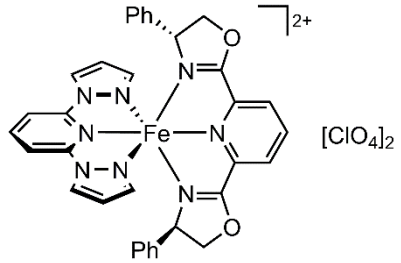
[Fe((*S*)-L^1*i*Pr)(bimpy)][ClO_4]$_2$ (**5**)



[2,6-*Bis*((*S*)-4-*iso*propyl-4,5-dihydrothiazol-2-yl)pyridine]-[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II) diperchlorate

$C_{36}H_{36}Cl_2FeN_8O_8S_2$

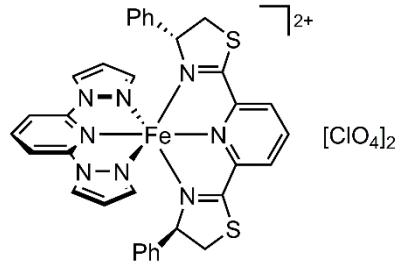
[Fe((*S*)-L^2*i*Pr)(bimpy)][ClO_4]$_2$ (**6**)



[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrooxazol-2-yl)pyridine]-[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II) diperchlorate

$C_{34}H_{28}Cl_2FeN_8O_{10}$

[Fe((*R*)-L^1Ph)(bpp)][ClO_4]$_2$ (**7**)

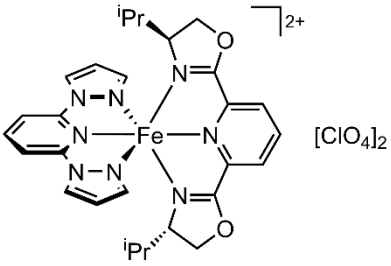


[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrothiazol-2-yl)pyridine]-[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II) diperchlorate

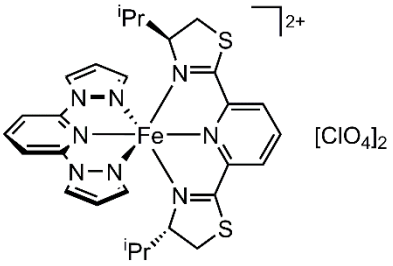
$C_{34}H_{28}Cl_2FeN_8O_8S_2$

[Fe((*R*)-L^2Ph)(bpp)][ClO_4]$_2$ (**8**)

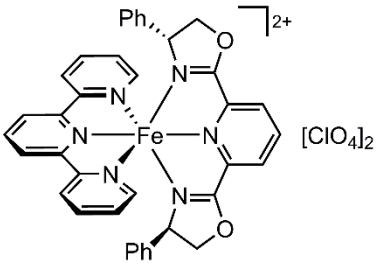
Complexes referred to in this study (continued)



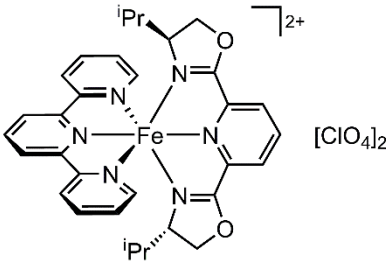
[2,6-*Bis*((*S*)-4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II) diperchlorate
$C_{28}H_{32}Cl_2FeN_8O_{10}$
[Fe((*S*)-L^1*i*Pr)(bpp)][ClO_4]$_2$ (**9**)



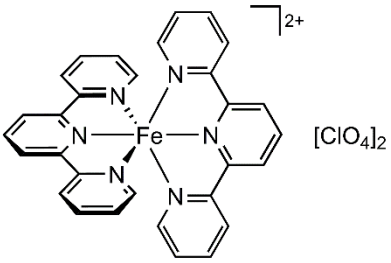
[2,6-*Bis*((*S*)-4-*iso*propyl-4,5-dihydrothiazol-2-yl)pyridine]-
[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II) diperchlorate
$C_{28}H_{32}Cl_2FeN_8O_8S_2$
[Fe((*S*)-L^2*i*Pr)(bpp)][ClO_4]$_2$ (**10**)



[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,2':6',2''-terpyridine]iron(II) diperchlorate
$C_{38}H_{30}FeCl_2N_6O_{10}$
[Fe((*R*)-L^1Ph)(terpy)][ClO_4]$_2$ (**11**)

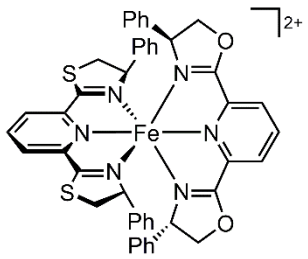


[2,6-*Bis*((*S*)-4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,2':6',2''-terpyridine]iron(II) diperchlorate
$C_{32}H_{34}FeCl_2N_6O_{10}$
[Fe((*S*)-L^1*i*Pr)(terpy)][ClO_4]$_2$ (**12**)

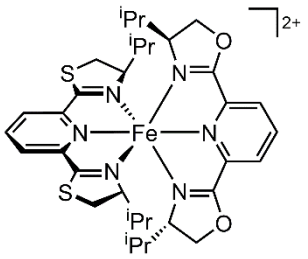


Bis[2,2':6',2''-terpyridine]iron(II) diperchlorate
$C_{30}H_{22}FeCl_2N_6O_8$
[Fe(terpy)$_2$][ClO_4]$_2$

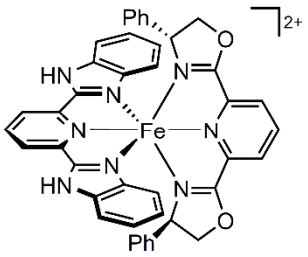
Complex cations studied by DFT calculations



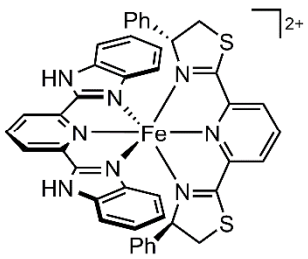
[2,6-*Bis*((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,6-*bis*((*R*)-4-phenyl-4,5-dihydrothiazol-2-yl)pyridine]iron(II)
$C_{46}H_{38}FeN_6O_2S_2$
$[Fe((S)\text{-}L^1Ph)((R)\text{-}L^2Ph)]^{2+}$ (**1**$^{2+}$)



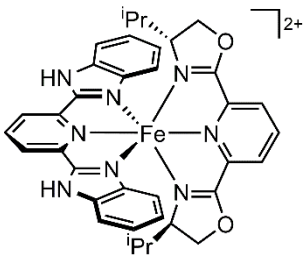
[2,6-*Bis*((*S*)-4-*iso*propyl4,5-dihydrooxazol-2-yl)pyridine]-
[2,6-*bis*((*R*)-4-*iso*propyl-4,5-dihydrothiazol-2-yl)pyridine]iron(II)
$C_{34}H_{46}FeN_6O_2S_2$
$[Fe((S)\text{-}L^1iPr)((R)\text{-}L^2iPr)]^{2+}$ (**2**$^{2+}$)



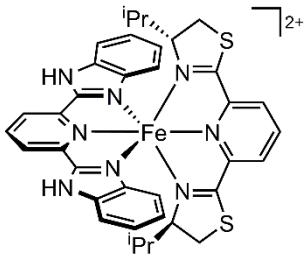
[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II)
$C_{42}H_{32}FeN_8O_2$
$[Fe((R)\text{-}L^1Ph)(bimpy)]^{2+}$ (**3**$^{2+}$)



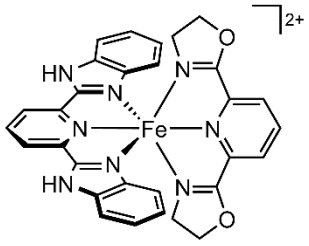
[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrothiazol-2-yl)pyridine]-
[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II)
$C_{42}H_{32}FeN_8S_2$
$[Fe((R)\text{-}L^2Ph)(bimpy)]^{2+}$ (**4**$^{2+}$)



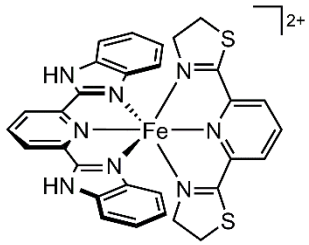
[2,6-*Bis*((*R*)-4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II)
$C_{36}H_{36}FeN_8O_2$
$[Fe((R)\text{-}L^1iPr)(bimpy)]^{2+}$ (**5**$^{2+}$)



[2,6-*Bis*((*R*)-4-*iso*propyl-4,5-dihydrothiazol-2-yl)pyridine]-
[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II)
$C_{36}H_{36}FeN_8S_2$
$[Fe((R)\text{-}L^2iPr)(bimpy)]^{2+}$ (**6**$^{2+}$)

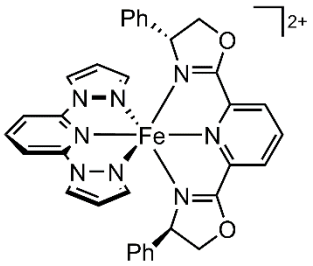


[2,6-*Bis*(4,5-dihydrooxazol-2-yl)pyridine]-
[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II)
$C_{30}H_{24}FeN_8O_2$
$[Fe(L^1H)(bimpy)]^{2+}$

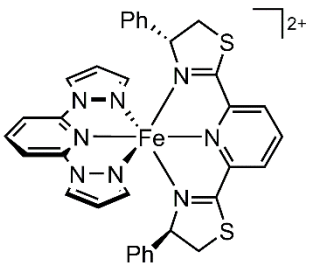


[2,6-*Bis*(4,5-dihydrothiazol-2-yl)pyridine]-
[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II)
$C_{30}H_{24}FeN_8S_2$
$[Fe(L^2H)(bimpy)]^{2+}$

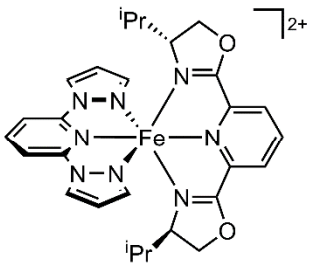
Complex cations studied by DFT calculations (continued)



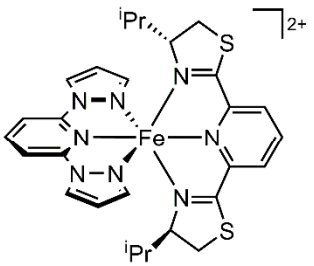
[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II)
$C_{34}H_{28}FeN_8O_2$
$[Fe((R)\text{-}L^1Ph)(bpp)]^{2+}$ (**7**$^{2+}$)



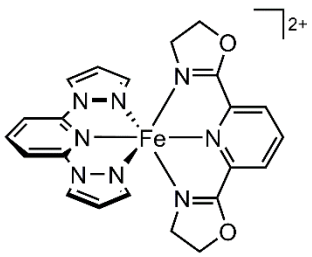
[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrothiazol-2-yl)pyridine]-
[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II)
$C_{34}H_{28}FeN_8S_2$
$[Fe((R)\text{-}L^2Ph)(bpp)]^{2+}$ (**8**$^{2+}$)



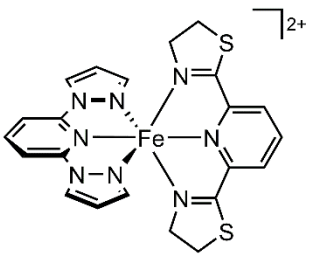
[2,6-*Bis*((*R*)-4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II)
$C_{28}H_{32}FeN_8O_2$
$[Fe((R)\text{-}L^1iPr)(bpp)]^{2+}$ (**9**$^{2+}$)



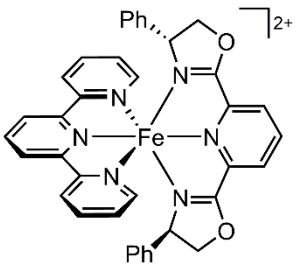
[2,6-*Bis*((*R*)-4-*iso*propyl-4,5-dihydrothiazol-2-yl)pyridine]-
[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II)
$C_{28}H_{32}FeN_8S_2$
$[Fe((R)\text{-}L^2iPr)(bpp)]^{2+}$ (**10**$^{2+}$)



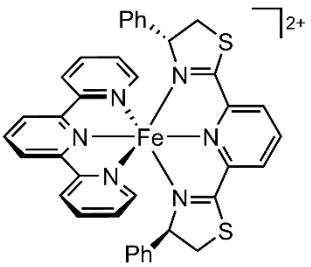
[2,6-*Bis*(4,5-dihydrooxazol-2-yl)pyridine]-
[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II)
$C_{22}H_{20}FeN_8O_2$
$[Fe(L^1H)(bpp)]^{2+}$



[2,6-*Bis*(4,5-dihydrothiazol-2-yl)pyridine]-
[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II)
$C_{22}H_{20}FeN_8S_2$
$[Fe(L^2H)(bpp)]^{2+}$

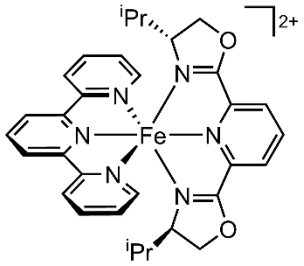


[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,2':6',2''-terpyridine]iron(II)
$C_{38}H_{30}FeN_6O_2$
$[Fe((R)\text{-}L^1Ph)(terpy)]^{2+}$ (**11**$^{2+}$)

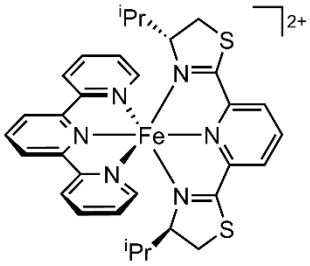


[2,6-*Bis*((*R*)-4-phenyl-4,5-dihydrothiazol-2-yl)pyridine]-
[2,2':6',2''-terpyridine]iron(II)
$C_{38}H_{30}FeN_6S_2$
$[Fe((R)\text{-}L^2Ph)(terpy)]^{2+}$

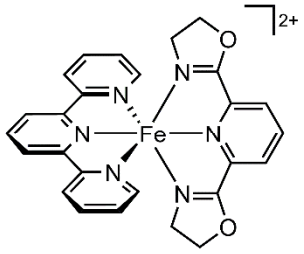
Complex cations studied by DFT calculations (continued)



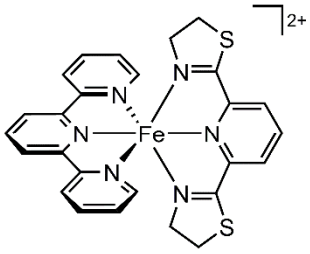
[2,6-*Bis*((*R*)-4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridine]-
[2,2':6',2''-terpyridine]iron(II)
$C_{32}H_{34}FeN_6O_2$
$[Fe((R)\text{-}L^1iPr)(terpy)]^{2+}$ (**12**$^{2+}$)



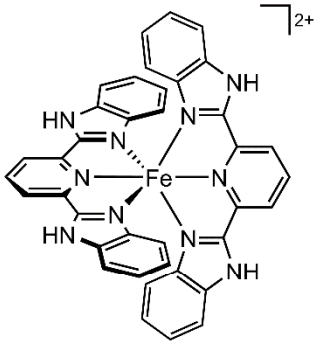
[2,6-*Bis*((*R*)-4-*iso*propyl-4,5-dihydrothiazol-2-yl)pyridine]-
[2,2':6',2''-terpyridine]iron(II)
$C_{32}H_{34}FeN_6S_2$
$[Fe((R)\text{-}L^2iPr)(terpy)]^{2+}$



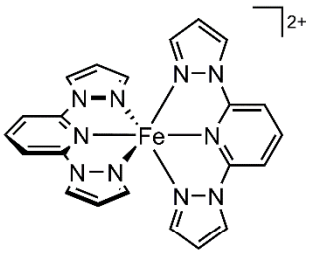
[2,6-*Bis*(4,5-dihydrooxazol-2-yl)pyridine]-
[2,2':6',2''-terpyridine]iron(II)
$C_{32}H_{34}FeN_6O_2$
$[Fe(L^1H)(terpy)]^{2+}$



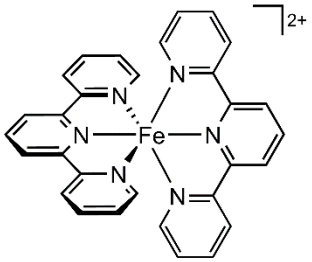
[2,6-*Bis*(4,5-dihydrothiazol-2-yl)pyridine]-
[2,2':6',2''-terpyridine]iron(II)
$C_{32}H_{34}FeN_6S_2$
$[Fe(L^2H)(terpy)]^{2+}$



Bis[2,6-*bis*(benzimidazol-2-yl)pyridine]iron(II)
$C_{38}H_{26}FeN_{10}$
$[Fe(bimpy)_2]^{2+}$



Bis[2,6-*bis*(pyrazol-1-yl)pyridine]iron(II)
$C_{22}H_{18}FeN_{10}$
$[Fe(bpp)_2]^{2+}$



Bis[2,2':6',2''-terpyridine]iron(II)
$C_{30}H_{22}FeN_6$
$[Fe(terpy)_2]^{2+}$