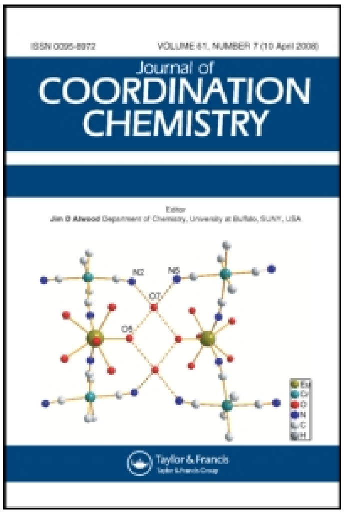

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ISOMER ELUCIDATION IN MONO- AND BINUCLEAR 1,4-DIISOCYANOBENZENE DERIVATIVES OF FERROUS BIS-NAPHTHOQUINONE DIOXIME

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The syntheses of mononuclear and binuclear derivatives of low spin ferrous naphthoquinone dioxime complexes containing the axial ligand 1,4-diisocyanobenzene (DIB) are described. Chromatographic separation and nmr characterization of sym and asym isomers of $Fe(NPQH)_2(Py)(DIB)$ as well as two of three possible isomers for $[Fe(NPQH)_2Py]_2(DIB)$ are described. Kinetic factors effecting the yields of mono *vs* binuclear species are elucidated.

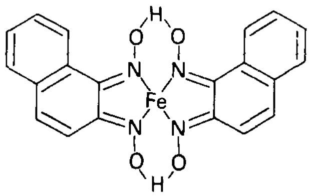
Keywords: Iron, Low-spin, complexes, 1,4-diisocyanobenzene, naphthoquinone dioxime

INTRODUCTION

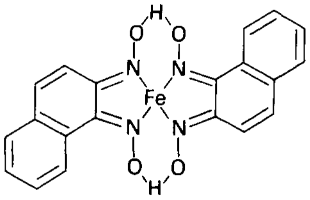
We have previously described a variety of low spin Fe(II) complexes[1] containing the 1,2-naphthoquinone dioximate ligand (NPQH) of the general form *trans*-$Fe(NPQH)_2XY$ where the axial ligands X and Y may be pyridine, imidazole, CO, phosphines, isocyanides, *etc.* The low symmetry of 1,2-naphthoquinone dioxime can in principle result in isomerism based on the symmetrical or asymmetrical disposition of the aromatic rings in the bis complexes. Reports of isomerism in square planar or trans octahedral derivatives of unsymmetrical bis dioximes or tetraimine ligands are surprisingly rare for first row transition metals. Early reports of cis-trans isomers of square planar bis-benzylmethylglyoximato nickel(II) proved to be due to different crystalline forms of only the trans isomer.[2] Only the trans (asym) isomer is typically formed in syntheses of metal complexes of tetraimine ligands derived from unsymmetrical diketones.[3,4]

The previously described derivatives of *trans*-$Fe(NPQH)_2XY$ all run as two identically coloured spots in TLC suggesting they are mixtures of isomers. During the course of purification of linear chain compounds[5] containing $Fe(NPQH)_2$ derivatives, it became both necessary and useful to separate these isomers. Here we report the separation and characterization of isomers in mono- and binuclear complexes containing the 1,4-diisocyanobenzene (DIB) ligand.

SYM



ASYM



EXPERIMENTAL

Materials

$Fe(NPQH)_2Py_2$ was prepared as described previously.[1] 1,4-Diisocyanobenzene was prepared by the reaction of the diformamide of *p*-phenylenediamine with phosgene.[6] νnc: 2127 cm^{-1}. Nmr, $CDCl_3$ 7.35.

Fe(NPQH)$_2$(Py)(DIB)

A degassed solution of 1 g (1.6 mmol) $Fe(NPQH)_2Py_2$ in 10% $CH_3OH/CHCl_3$ was added to a 10-fold excess of DIB in chloroform. The solution was stirred at room temperature for 15 minutes and then petroleum ether was added to induce precipitation. The crude product was chromatographed on silica gel ($CHCl_3$ eluant) to remove excess DIB and the DIB-free fraction concentrated. The final product was recrystallized twice from $CHCl_3$/petroleum ether. Nmr, see Figure 1. IR, νnc 2110 cm^{-1}. Vis, 540 nm, 395 nm(sh).

[Fe(NPQH)$_2$Py]$_2$(DIB)

The procedure is the same as above except a mole ratio of 1 DIB to 2 $Fe(NPQH)_2Py_2$ and a one hour reaction time is used. The chromatographic step is unnecessary. The absence of available isocyanide binding sites in the product may be checked

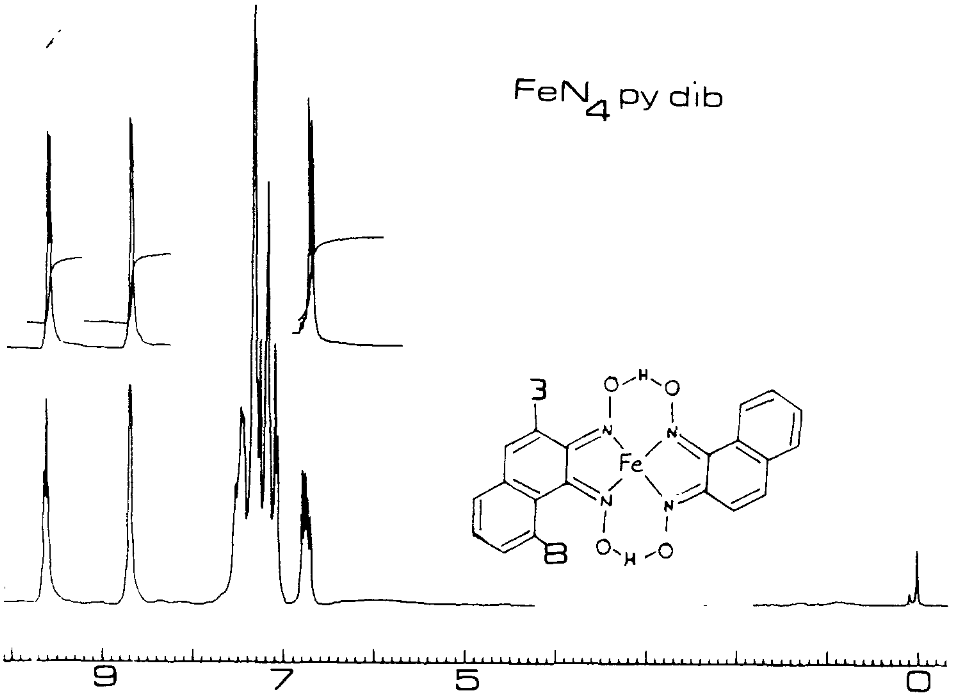


FIGURE 1 Proton NMR Spectra (300 MHz, $CDCl_3$) of isomeric mixture of $Fe(NPQH)_2(Py)(DIB)$ (lower) and an isomerically pure fraction assigned to the asym isomer (upper). The isomerically pure sym isomer (not shown) gives a spectrum identical to the asym isomer except H8 and H3 are shifted upfield .03 and .05 ppm respectively.

spectrophotometrically by titration with $Fe(NPQH)_2Py_2$. The absence of an absorbance increase at 540 nm over ten minutes at room temperature in chloroform solution on adding $Fe(NPQH)_2Py_2$ (λmax 702 nm) indicates the absence of available sites. NMR, Figure 2. IR, νnc 2106 cm^{-1}. Vis, 540 nm, 395 nm (sh).

Spectrally identical fractions from chloroform elution on a silica gel column were collected. Fractions giving single spot TLC were identified by nmr. Visible spectra were recorded on an Aminco DW2A instrument. Proton nmr were run on a Bruker AM300 in $CDCl_3$ with TMS as internal standard. Satisfactory elemental analyses were obtained on new compounds by Canadian Microanalytical Service Ltd., Vancouver, B.C.

RESULTS AND DISCUSSION

Mono- vs *Binuclear Complexes*

The relative yields of mono- *vs* binuclear product is a strict function of the trapping of the pentacoordinate intermediate in the dissociative substitution reaction.

$$\begin{tikzcd}
 & & \underset{\mathrm{I}}{\mathrm{Fe(NPQH)_2(Py)(DIB)}} \\
\mathrm{Fe(NPQH)_2Py_2} \arrow[r, "k_{-py}"'] & \mathrm{Fe(NPQH)_2Py} \arrow[ur, "{k_{+DIB}[DIB]}"] \arrow[dr, "{k_{+I}[I]}"'] & \\
 & & \mathrm{[Fe(NPQH)_2Py]_2DIB}
\end{tikzcd}$$

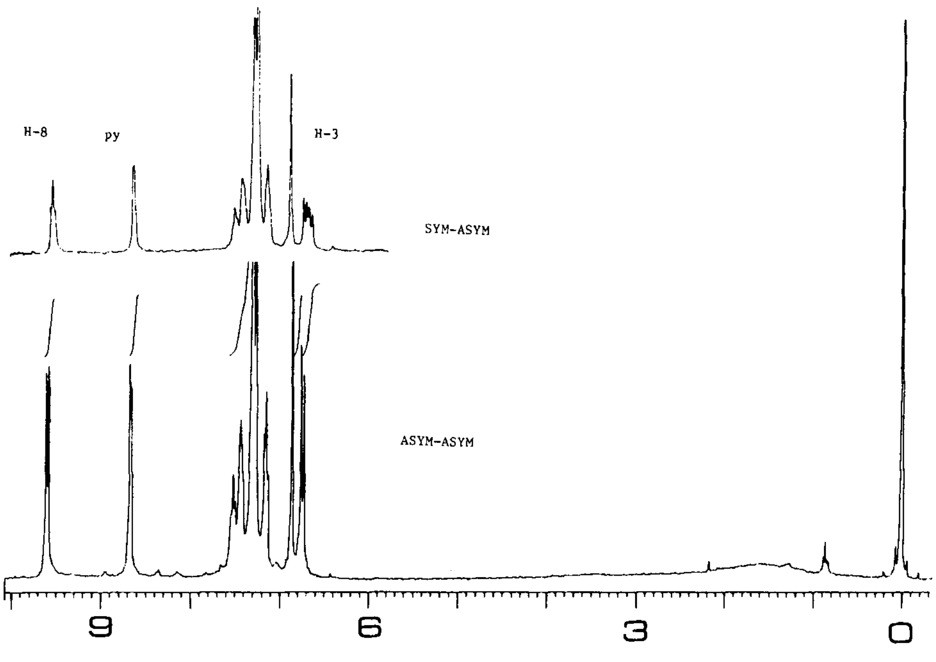


FIGURE 2. Proton NMR Spectra (300 MHz, $CDCl_3$) of isomerically pure samples of binuclear $[Fe(NPQH)_2Py]_2(DIB)$. The fast eluting isomer (below) is tentatively assigned asym-asym and the second chromatographically pure fraction assigned to the sym-asym isomer. The third slowest eluting sym-sym isomer could not be obtained free of the middle isomer but appears as a distinct spot in TLC.

TABLE I
Theoretical Yields of Mono- *Vs* Binuclear Complexes assuming statistical kinetics[a]

DIB/Fe	Mononuclear	Binuclear
0.5	0.0	0.50
0.75	0.34	0.33
1.0	0.52	0.24
2.0	0.76	0.12
5.0	0.90	0.05
10.0	0.95	0.024

[a] Yields are expressed as mole fractions of total Fe. By weight, the binuclear fraction is approximately double the value shown, giving net 100% yield in all cases.

Both axial ligands in the products are inert on the time scale of the synthetic reaction ($k_{-py} = 7.4 \times 10^{-2}$ s^{-1}).[1] Assuming a statistical effect only ($k_{+DIB} = 2k_{+I}$), the relative yields of mono *vs* binuclear product may be calculated (Table I). The values in Table I are consistent with qualitative observations based on TLC spot intensities for the product of a reaction using ratios of DIB/Fe of 3,0.5 (exclusively binuclear), and 10 (> 90% mono).[7] The monomer and dimer are spectrally and kinetically similar. However the monomer contains an available isocyanide ligand which is easily identified spectrophotometrically by reaction with another iron complex.

Isomers

Thin layer chromatography of the $Fe(NPQH)_2XY$ complexes described previously[1] results in two spots of identical colour and intensity. By way of contrast, corresponding higher symmetry dimethylglyoxime[8] and benzoquinone dioxime[1] analogues run as a single spot.

Column chromatography was used to separate the isomers of $Fe(NPQH)_2(Py)(DIB)$. The faster eluting isomer is tentatively assigned to the asym- isomer and the slower one assigned to the sym- isomer. The separate isomers are indistinguishable by their visible spectra in chloroform; both show an MLCT band at 540 nm and a ligand band at ~395 nm. However, the MLCT band extinction coefficient for the faster eluting isomer is 1.0×10^4 M^{-1} cm^{-1} but 1.9×10^4 M^{-1} cm^{-1} for the other isomer. A lower ε is expected for the centrosymmetric asym isomer (ignoring the axial ligands).

The nmr spectra show distinct differences between the two isomers (Figure 1). Axial ligand resonances are identical. However, the H-8 proton of naphthoquinone[9] is .03 ppm further down field in the asym isomer. This proton appears as a doublet ($J_{7,8} = 8$ Hz) in each isomer but is a pseudo-triplet in a mixture of the two. The high field resonance at 6.7 ppm assigned to H-3 is also .05 ppm further downfield in the asym isomer. We attribute the chemical shift differences to changes in the orientation of these protons *vis-à-vis* the N=O bond as a result of different distortions of the complex to relieve the steric interactions of H-8 and O in the two isomers.

The binuclear complex $[Fe(NPQH)_2py]_2(DIB)$ runs on TLC as 3 spots (intensity ratio 1 : 2 : 1) consistent with the pattern expected for the isomers sym-sym, sym-asym, and asym-asym. Chromatography afforded isomerically pure samples of two of the three possible isomers based on nmr (Figure 2). The isomeric mixture gives unresolved multiplets for the 8 and 3 protons. However, the first band off the column gives a clean doublet at the lower field position for both H8 and H3. This isomer is tentatively assigned the asym-asym structure. A second pure isomer (based on single spot TLC) shows a pseudo triplet for H-8 (assigned to overlapping doublets for asym and sym naphthoquinones) and a clear pair of equally intense doublets for H-3 consistent with the asym-sym isomer.

The sym and asym isomers do not give rise to appreciable differences in intramolecular or axial ligation effects. However they would show dramatically different properties with respect to intermolecular interactions in linear chain derivatives.

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REFERENCES

1. N. Siddiqui and D.V. Stynes, *Inorg. Chem.*, **25**, 1982 (1986).
2. K.A. Jensen, B. Nygaard and R.B. Jensen, *Acta Chem. Scand.*, **19**, 770 (1965).
3. D.S. Eggleston and S.C. Jackels, *Inorg. Chem.*, **19**, 1593 (1980).
4. N.K. Kildahl, G. Antonopolous, N.E. Fortier and W.D. Hobey, *Inorg. Chem.*, **24**, 429 (1985).
5. P. Lefko and D.V. Stynes, Submitted for publication.
6. I. Ugi, German Patent 1158500 (1963), app. 1962; **CA** *61*:8243 (1964).
7. Because of the multiple spots due to isomers, the TLC observations of mono- *vs* binuclear product yields are based on the analogous $Fe(DMGH)_2$ complexes.[5]
8. X. Chen, and D.V. Stynes, *Inorg. Chem.*, **25**, 1173 (1986).
9. W.B. Smith, D.L. Deavenport and A.M. Ihrig, *J. Am. Chem. Soc.*, **94**, 1959 (1972).