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Spectral evidence for two bridging cyanide modes in the coordination of cyanide anion into the Br[Fe^{III}/Cu^{II}diporphyrin] complex in chloroform

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Abstract—The heterodinuclear Br(Fe^{III}TTP-*o*-$O(CH_2)_2O$-*o*-TTPCu^{II}) complex (**1**) (TTP-*o*-O = 5-(*o*-hydroxy)-10,15,20-tritolylporphyrin dianion) has been synthesized. The porphyrins have been linked via flexible spacer–diether moiety attached to *ortho*- positions of *meso*-phenyls. The coordination of cyanide anion by **1** has been studied by ^1H NMR, IR, UV–vis, and EPR spectral methods in chloroform solution. Two dinuclear isomeric complexes; $[(NC)Fe^{III}\text{-}CN\text{-}Cu^{II}]^-$ and $[(NC)Fe^{III}\text{-}NC\text{-}Cu^{II}]^-$, containing bridging cyanide ligands have been found in the solution on the basis of IR and NMR assignments and the comparison of the results with previously studied equilibria in CN^- : $[(Fe^{III}TTP\text{-}o\text{-}O(CH_2)_2O\text{-}o\text{-}TTPFe^{III})]^{2+}$ system. © 1997 Elsevier Science Ltd

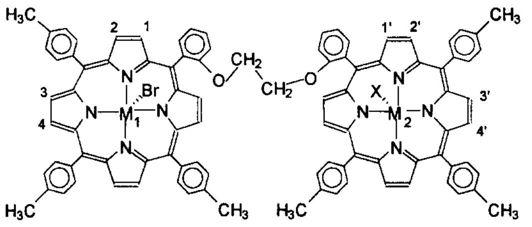
Keywords: heterodinuclear diporphyrin; Fe^{III}/Cu^{II} complex; cyanide coordination; bridging cyanide; NMR; IR.

Diporphyrins provide a particular opportunity to fix two metal centres in spatial proximity by the choice of an appropriate link between adjacent porphyrin macrocycles. Homo- and heterobimetallic diporphyrins are useful biomimetic models for some enzymatic systems like cytochrome c oxidases or photosystem II [1–3]. The work on face-to-face (FTF) diporphyrins [4–11] and pillared diporphyrins [12–22] resulted in finding the catalytic properties of biscobaltodiporphyrins to reduce O_2 and H_2O_2 to H_2O, and catalytic ability of dismutation of H_2O_2 by bismanganesediporhyrins [6–8,11 and 20–22]. In diporphyrins of FTF, pillared, and gable [23] type, the spacer(s) adjacent to peripheral β- and/or *meso*-positions of porphyrin core allow the tuning the interporphyrin distance and geometry. The diporphyrins and their metal complexes with flexible spacers were also studied in details [24–28]. *Bis*-metallodiporphyrins are particularly reactive in activation of small molecules like O_2, H_2, N_2 [1]. They are also photoactive [29,30] to a larger extent than their monomeric analogues and both mentioned aspects have been explored in studies for over the last two decades. Consequently, the elucidation of the basic coordination properties of those bimetallic systems is an important issue [25–28].

In previous paper we have demonstrated the coordination equilibria, cyanide bonding isomers, including a bridging mode for the series of diiron(III)–diporhyrin complexes in organic solvents [28]. This paper deals with the similar study on heterobimetallic analogue of that system, namely Fe^{III}/Cu^{II} diporphyrin: cyanide one. The preferential insertion of those two metal ions into the diporphyrin was consistent with presence of such a bimetallic assembly in cytochrome c oxidase enzyme, containing heme iron and non-heme copper centres. The enzyme catalyses four-electron/four H^+ reduction of molecular oxygen to water. A large variety of models of that natural dinuclear heterobimetallic system were synthesized and studied [31–43]. In those structurally characterized complexes the iron was coordinated to porphyrin macrocycle, whereas the copper centre was bound to three- or four-donor ligands of variable coordination geometry. The two metal centres were bridged by an oxygen atom [31], a cyanide [32–35], and other ligands [36–42].

The cyanide is known to bind to the cytochrome c oxidase metal centre(s) [34]. In the model studies cyanide was found to bind as bridging ligand, with carbon coordinated to Fe^{III} and nitrogen bound to Cu^{II} metal ions [32–35]. Similar coordination geometry was postulated for the resting state of enzyme although bridging isomer with Fe^{III}-NC-Cu^{II} assembly should be considered as well.

In the system under study both Fe^{III} and Cu^{II} are inserted into the 5-(phenyl)-10,15,20-*tris*(*p*-methylphenyl)porphyrin subunits covalently linked by flexible ethylene spacer attached *via ortho*-oxygen atoms to *meso*-phenyls. Spectral characteristics based on IR, UV–vis, NMR and ESR methods enabled a close insight into the coordination properties of this particular bimetallic complex.



1 M_1 = Fe(III), M_2 = Cu(II), no X

2 M_1 = M_2 = Fe(III), X = Br$^-$

EXPERIMENTAL

Synthesis of complexes

Br(Fe^{III}TTP-*o*-O-(CH$_2$)$_2$-O-*o*-TTPCu^{II}) (**1**). The (H$_2$TTP-*o*-O(-CH$_2$)$_2$-O-*o*-TTPH$_2$) diporphyrin was synthesized as described previously [28]. The Cl(Fe^{III} TTP-*o*-O-(CH$_2$)$_2$-O-*o*-TTPH$_2$) complex was obtained by dropwise addition of methanolic solution of iron(II) dichloride (35.5 mg, 0.28 mmol in 5 ml methanol) into the chloroform solution of diporphyrin (251 mg, 0.195 mmol) refluxed under nitrogen atmosphere. The mixture containing non-metallated, mono-metallated and bis-metallated diporphyrins was chromatographed on silicagel to remove starting materials. Metal-free porphyrin (30 mg, 0.023 mmol and about 25 mg of products of degradation) were easily eluted from basic alumina with methylene dichloride, whereas all porphyrin complexes with Fe^{III} needed the 1% methanol/methylene dichloride eluent. Copper(II) was inserted into mono-ferric diporphyrin complex by addition of excess of copper(II) dichloride into the mixture of mono- and *bis*-Fe^{III}–diporphyrin complexes using the same combination of solvents as in the previous step. The HO(Fe^{III}TTP-*o*-O(CH$_2$)$_2$-O-*o*-TTPCu^{II}) was eluted with 0.5% methanol/methylene dichloride as first band (110 mg, 0.073 mmol), the second band was intramolecular μ-oxo (Fe^{III})$_2$ diporphyrin (105 mg, 0.070 mmol). The HO(Fe^{III}TTP-*o*-O-(CH$_2$)$_2$-O-*o*-TTPCu^{II}) complex was then converted into **1** by the extraction of methylene dichloride solution of hydroxo-complex with 0.2 M HBr(aq) (112 mg, 0.071 mmol, yield 36%). Anal. Calcd. for BrCuFeC$_{96}$H$_{70}$N$_8$O$_2$; C 73.95; H 4.50; N 7.15. Found: C 74.01; H 4.52; N 7.10. MS: 1568,1566 [1+H]$^+$. UV–vis: Soret bands: 417 nm (17,090), 433 nm (14,550), Q-bands: 540 nm (1056), 513 nm (sh, 790), 588 nm (515), 694 nm (sh, 175).

Br(Fe^{III}TTP-*o*-O-(CH$_2$)$_2$-O-*o*-TTPFe^{III})Br (**2**). **2** was prepared from Cl(Fe^{III}TTP-*o*-O-(CH$_2$)$_2$-O-*o*-TTPFe^{III})Cl by the conversion of it into μ-oxo complex on basic alumina followed by extraction of methylene dichloride solution of the latter with 0.2 M HBr(aq) [28].

Methods and reagents

^{1}H NMR spectra were collected on Bruker AMX spectrometer operating at 300 MHz in the quadrature mode over a 45,000 Hz spectral window with 16 K data points, 300–1000 transients for experiment, and 250 ms prepulse delay. The free induction decay (FID) was apodized using exponential multiplication which induced 5–50 Hz broadening depending on the natural line width. The residual ^{1}H resonance of the deuterated solvent was used as a secondary reference. The UV–vis spectra were recorded on the HP 8453 diode-array spectrophotometer. The infrared spectra were measured with a Bruker IFS113V spectrophotometer in 3 mm path length fluorite cells. In the titration procedure the starting concentrations of chloroform solutions of **1** and **2** were 0.015 M. The EPR experiment was performed with Bruker ESP 300E spectrometer at X-band. The mass spectrum of **1** was obtained at Finnigan MAT TSQ 700 spectrometer by Electro-Spray Ionization method at 4.5 kV ionization potential and 250°C capillary temperature. The solvent was acetonitrile/1% trifluoroacetic acid. In NMR and EPR titrations the starting concentration of **1** in CDCl$_3$ was 0.01 M and 0.4 M tetrabutylammonium cyanide ([TBA][CN]) was used. The solvents were freshly distilled and additionally the chloroform used to prepare the solutions for spectral measurements was passed through basic alumina prior to use.

RESULTS

Characterization of **1**

The attempts to obtain the complex **1** by condensation of premetallated halves failed due to the inhibition of reaction between metallated (as either Zn^{II} or Cu^{II} complex) mono-hydroxoporphyrin and its 2-bromoethyloxy-derivative in dimethylformamide in a presence of potassium carbonate, the procedure operating in case of metal-free porphyrins [24]. Therefore, the complex was synthesized using the consecutive metallation with iron and copper metal ions. Passing the Xiron(III)porphyrins (X = halogen anion) through basic alumina leads to conversion of high-spin iron(III) complexes into the μ-oxo dinuclear complexes [44,45]. It is not the case for Fe^{III}/Cu^{II} diporphyrin complex studied here, which can be eluted from intermediate activity basic alumina with methylene dichloride as OH(Fe^{III}TTP-*o*-O-$(CH_2)_2$-O-*o*-TTPCu^{II}). The chromatography on silicagel preserved the bromide ion in **1** to substitute for any other. Due to that difference in chromatographic mobility the mixed-metal complex could be separated from diiron(III) impurity at the final step of synthesis. At this point it is worthy to mention that bridging anions Cl^- and OH^- were found in other dinuclear Fe^{III}/Cu^{II} complexes [36–38,42]. Thus, the bromide anion in **1** and hydroxide anion in OH(Fe^{III}TTP-*o*-O-$(CH_2)_2$-O-*o*-TTPCu^{II}) are bound stronger than those in mononuclear iron(III)porphynate complexes. For instance, the (TTPFe^{III})OH spontaneously converts into $(TTPFe^{III})_2O$ in organic solvents (where TTP is 5,10,15,20-tetra(*p*-methylphenyl)porphynato dianion) [44]. Also the complex **2** loses bromide and/or hydroxide ions during passing through basic alumina or upon extraction with 0.1 M NaOH(aq) and produces intramolecular μ-oxo complex [28]. The comparison of those properties of **1** and the compounds mentioned implies the intramolecular bridging coordination mode of simple anions like bromide anion in **1**.

The UV–vis spectrum of **1** presented in Fig. 1 is compared to the superposition of spectra of Br(Fe^{III} TTP) and Cu^{II}TTP complexes. The remarkable red shift of Soret band due to iron(III)porphyrin half, diminished extinction coefficient of Soret band of copper(II)porphyrin half, and red shift of Q-bands are indicative of rather substantial intramolecular interaction between two porphyrins [46–49]. In case of the metal-free diporphyrin no shift of Soret band has been observed [24]. However, the EPR spectrum of **1** (not presented) consists of typical high-spin iron(III) signal at $g = 6$ and broadened feature from copper(II) centre, typical for Cu^{II}porphyrin complexes [50] indicating that no strong magnetic coupling between two paramagnetic centres in **1** is present.

The ^1H NMR spectrum of **1** indicates the presence of two metal centres: high-spin iron(III) and copper(II). As can be expected [51], the spectrum consists of pyrrole resonances centred at 82 ppm (Fig. 2, trace A) and unresolved group of peaks from *p*-tollyl and phenyl resonances originated from iron-coordinated diporphyrin half, broad, overlapping resonances from copper-coordinated porphyrin core, and finally the resonances from bridging substituted ethane spacer. The unresolved feature from copper half is consistent with the previous observation by Godziela and Goff [52]. In case of Cu^{II}tetraarylporphynates the ^1H NMR spectra consist of broad resonances in the region of 8–7 ppm (for instance the spectrum of TPPCu(II) complex revealed the signals of *ortho* (7.48 ppm, 144 Hz bandwidth), *meta* (7.30 ppm, 32 Hz bandwidth), *p*-methyl (2.52 ppm, 10 Hz bandwidth) and broad, considerably paramagnetically shifted β-pyrrole resonance (visible only at ^2H NMR due to lower gyromagnetic ratio for ^2H) at 41 ppm (bandwidth 1150 Hz) [52].

Cyanide complexes

The starting complex **1** was titrated with [TBA][CN] in chloroform solutions and the reaction was monitored spectrally by ^1H NMR, IR, and UV–vis methods. The ^1H NMR spectroscopy allows to recognize the spin/ligation/oxidation states of the ironporphyrins [51]. The β-pyrrole resonance shift dramatically from 80 ppm to -15 ppm upon high-spin to low-spin conversion of Fe^{III}–tetrarylporphyrins. The spin-state conversion requires

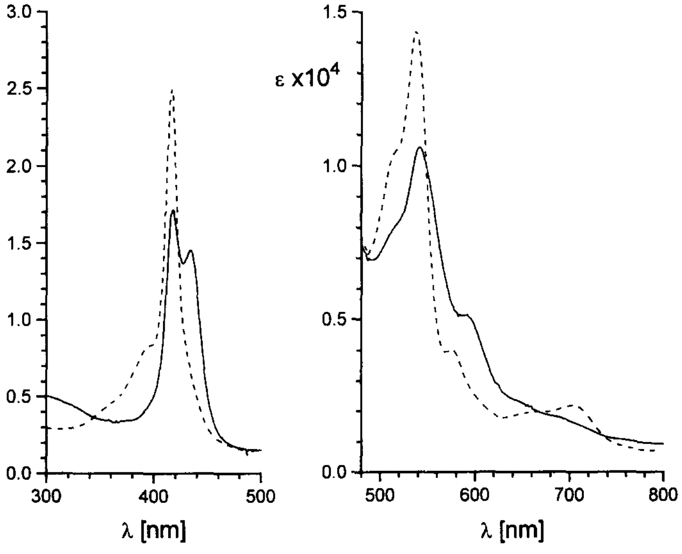


Fig. 1. UV–vis spectrum of **1** (solid line) and superimposed spectrum $TTPCu^{II}$ + $(TTPFe^{II})$Br (dashed line) in chloroform, normalized to extinction coefficient.

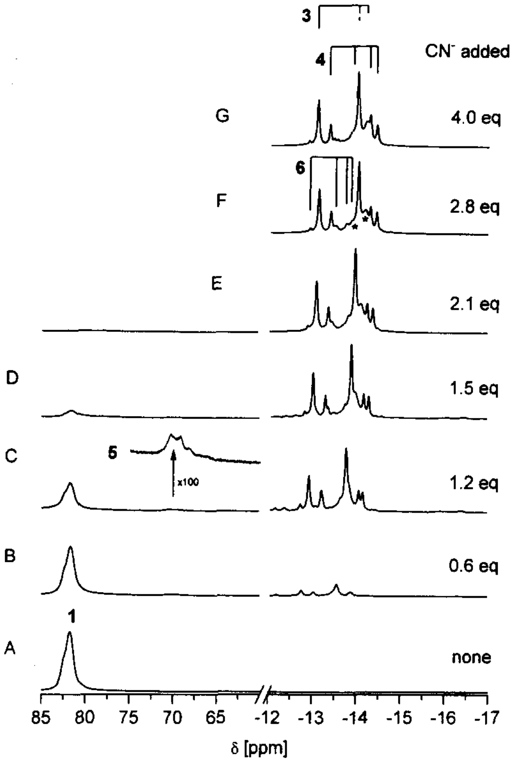


Fig. 2. The regions of β-pyrrole resonances of ^{1}H NMR spectra of solutions containing **1** and the indicated numbers of equivalents of [TBA][CN].

axial coordination of two ligands. Intermediate shifts are observed for intermediate spin-state or in case of chemical exchange between two or more states [53].

The method is much less informative in case of copper^{II}–porphyrins where the paramagnetic shifts are smaller and the bandwidths are much larger [52]. The ^{1}H NMR spectral monitoring of reaction between [TBA][CN] and **1** is illustrated in Fig. 2 A–G. Addition of 0.6 CN$^-$ equivalent into the CDCl$_3$ solution of **1** resulted in formation of low-spin Fe(III) complexes **3** and **4** with characteristically upfield shifted pyrrole resonances in the region of -12 to -15 ppm and trace amount of a new high-spin complex **5** (four, separated pyrrole resonances at about 70 ppm) (Trace C). The increase of cyanide concentration to twice that of **1** resulted in disappearance of resonance originated from high-spin complexes (Trace E). In the region of low-spin Fe^{III}–porphyrin pyrrole resonances the complicated pattern is seen. The spectrum is dominated by two sets of four-pyrrole resonances, which are partially overlapped. The integral intensity and deconvolution procedure showed that one of pyrrole resonances of species **3** is broader (the most upfield shifted) than other three ones. The pyrrole resonances from species **3** and **4** are partially overlapped. A minor species **6** is also present throughout the entire range of ligand concentration (traces B–G). The chemical shifts are dependent on cyanide anion concentration and the most sensitive is broad signal of **3**. This suggests that the resonance belongs to the β-pyrrole hydrogen close to the copper(II) centre which induces dipolar broadening of the signal. Since the chemical shift of low-spin pyrrole resonances of cyanide complexes formed in reaction with **2** did not show the variable chemical shift upon the change in cyanide concentration [28] the [CN]-dependent chemical shift of pyrrole resonances for **3** and **4** can only be interpreted in terms of changes in coordination sphere of Cu^{II}. The possible coordination equilibria will be discussed later.

UV–vis spectral monitoring demonstrates that no isosbestic points are present throughout the cyanide concentration used (Fig. 3). The most dramatic change can be observed at an early stage of titration, when the substantial decrease of the intensity of Soret band at 433 nm is observed, accompanied by the increase of the band centred at 417 nm and developing of new bands in the region of Q-bands. A further increase of cyanide anion concentration induces changes with separable isosbestic points which are lost upon the addition of a large excess of cyanide. Summarising, due to multicomponent equilibria in the system only the qualitative spectral picture is provided by that method.

Infrared spectroscopy serves more specific opportunity, particularly because chloroform is transparent within the region of ν(CN). It has been recognised very early that the stretching frequencies of cyanide ligand in IR spectroscopy are diagnostic of coordination mode of that ligand [54]. The increase of ν(CN) frequency upon coordination is due to the reduced electron density on *sp* σ* MO of cyanide, the orbital contributed mostly by carbon atom, more basic than nitrogen. The latter prevails in a contribution into the lower energy σ* MO [54]. The terminal binding of cyanide results in 20–30 cm^{-1} shift to higher wavenumbers, whereas bridging induces at least 20 cm^{-1} larger shift. The shift of ν(CN) upon bridge formation is influenced by both electronic and kinematic effect [55]. The latter comes from the physical constraint at the cyanide nitrogen site and shifts the ν(CN) to higher frequency without changing the force constant of the CN bond. The electronic effect is mainly due to bond formation in which cyanide nitrogen uses its antibonding σ* orbital for donation, which strengthen the CN bond. Thus, both effects shift the ν(CN) to a higher frequency upon bridge formation. The substantial coordination shift of ν(CN) upon bridging is general and was observed for the series of cyanide-bridged dinuclear complexes of iron, chromium, molybdenum, tungsten and manganese cations with Cp (cyclopentadienyl anion), CO, dppe (bis(diphenylphosphine)ethane) as additional ligands, where the bridging shift was 20–45 cm^{-1} higher in comparison with mononuclear subunits [55].

The series of papers by Holm and coworkers [34,45] on dinuclear Fe^{III}/Cu^{II} complexes with cyanide bridging ligand allowed to find the subtle relationship between structural details of bridging mode of that

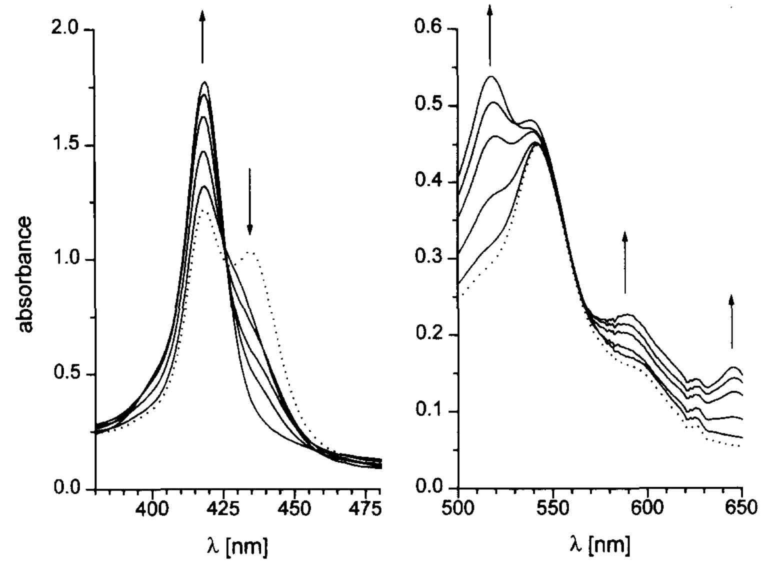


Fig. 3. The UV–vis spectral changes accompanying the addition of [TBA][CN] into **1** (0.7×10^{-4} M for Soret band region, 0.1 cm cell—left part of the figure and 0.4×10^{-4} M for Q-bands region, 1 cm cell—right part of the figure). The spectrum of the starting complex is represented by dotted line. The changes corresponding to the addition of [TBA][CN] equivalents are marked with arrows. The number of [TBA][CN] equivalents per **1** were: 0.6; 1.2; 2.2; 4; 25.

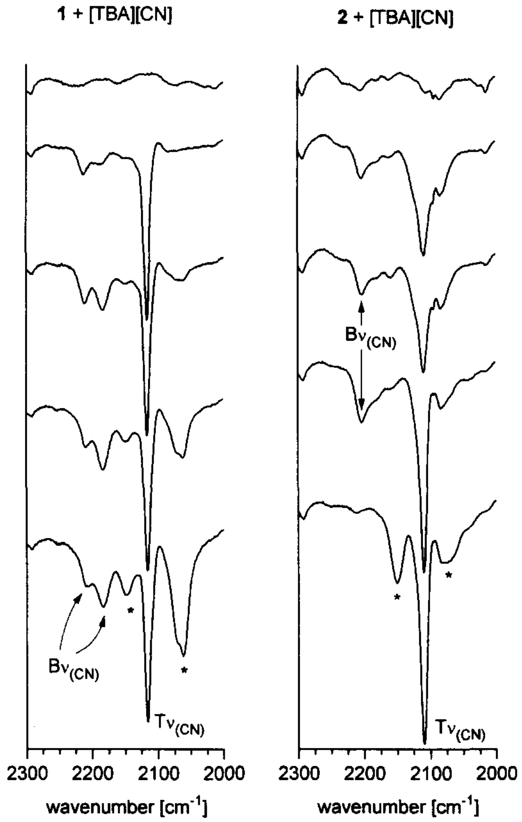


Fig. 4. The IR spectra of chloroform solutions containing **1** (left column) and **2** (right column) and [TBA][CN] at the concentrations (from top to bottom): 0; 0.6; 1.2; 2.2; and 4.1 equivalents of cyanide per **1** (**2**). The bridging stretching cyanide vibrations are marked as Bν(CN) while those originated from terminal cyanides are marked by Tν(CN). The bands from 'free' cyanide are marked with asterisks.

ligand and ν(CN) stretching frequency, which fall into region of 2120–2183 cm^{-1} [34,35].

Figure 4 shows the ν(CN) bands for two cases: $(Fe^{III})_2$diporphyrin **2** and Fe^{III}/Cu^{II}diporphyrin **1**. The structure of the dinuclear cyanide complexes of **2** has been established on the basis of NMR measurements [28]. The formation of intramolecularly cyanide-bridged species NC–Fe(III)–CN–Fe(III)–CN was found for **2** and the appearance of the band corresponding to bridging stretching Bν(CN) at 2203 cm^{-1} with further disappearance of it upon further increase of cyanide ion concentration up to four-fold excess in relation to **2** was consistent with NMR assignments. The stretching corresponding to terminally coordinated cyanide is present at 2109 cm^{-1} throughout the entire range of cyanide anion concentration and originates both from terminal cyanides in NC–Fe(III)–CN–Fe(III)–CN and $(NC)_2(Fe^{III}$ TTP-*o*-$O(CH_2)_2O$-*o*-$TTPFe^{III})(CN)_2$. In case of **1**, two different ν(CN) stretchings in the bridging region are observed at 2185 and 2212 cm^{-1} and they are still present even when [CN] concentration grows 10 times higher than that of **1**. The strong band at 2116 cm^{-1} corresponding to terminal cyanide is observed throughout entire range of cyanide anion concentration.

EPR titration showed that the well resolved spectrum of Cu(II) with $g_{\parallel} = 2.17$, $g_{\perp} = 2.06$, $A_{\parallel} = 206$ Gs, and $A_N = 18$ Gs, and low-spin Fe^{III} feature with only one separated signal at $g = 1.62$ is formed at the early stage of titration accompanied by signal at $g = 6$ due to starting **1**. The final spectrum obtained for the solution of **2** with ten-fold excess of cyanide is presented at Fig. 5. The high amplitude radical signal at $g = 2$ is due to side reaction, usually observed in

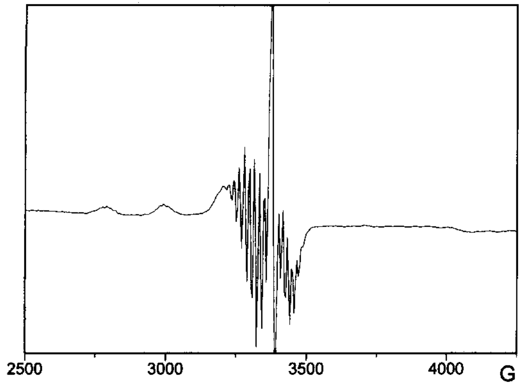
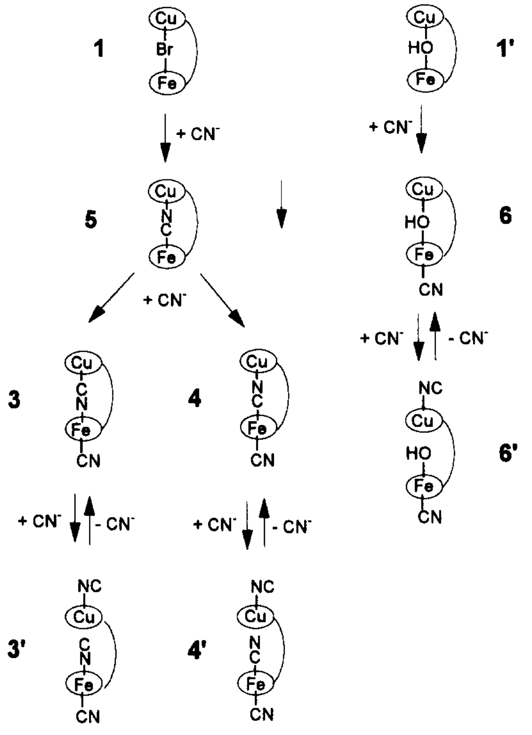


Fig. 5. The EPR spectrum of the chloroform solution containing **1** and 0.05 M [TBA][CN] recorded at 77K.

case of metalloporphyrins [56]. High resolution of Cu^{II} feature suggests the copper centre is magnetically isolated contrary to the **1**.

In some model dinuclear Fe^{III}/Cu^{II} complexes, the magnetic coupling between paramagnetic centres leads to the characteristic $S = 1$ spectra, observed by Murray and coworkers [32]. For the natural cytochrome c oxidase both resting state and its cyanide form are EPR silent [57].



Scheme 1.

DISCUSSION

The heterodinuclear Br(Fe^{III}TTP-*o*-$O(CH_2)_2O$-*o*-TTPCu^{II}) complex contains the bromide anion which is not lost upon chromatography on silicagel. The UV–vis spectrum of **1** shows a substantial interaction of the exciton-type between two metalloporphyrin subunits. Also the broadened feature attributed to Cu^{II} centre in EPR spectrum is consistent with the picture according to which a bromide anion bridges two metal centres.

The addition of [TBA][CN] into **1** at the concentration twice higher than that of **1** causes the disappearance of high-spin complexes and instead two major complexes **3** and **4** are formed. Both of them contain two cyanide anions coordinated with the iron(III) low-spin centre. The IR spectra indicate the presence of both terminal and bridging cyanides. Moreover, there are two different stretchings in the region of bridging frequencies. The above observations demonstrate clearly that two different dinuclear complexes containing bridging and terminal cyanide ligands are formed (**3** and **4** in Scheme 1). They remain major species even at the presence of a large excess of cyanide ligand. The concentration dependence of a chemical shift in ^1H NMR spectra of **3** and **4** suggests that the Cu^{II} centre is involved in an additional equilibrium with an external cyanide anion. Indeed, large excess of cyanide induces additional changes in UV–vis spectra observed clearly in the region of Q-bands. This implies that species **3** and **4** are in equilibrium with **3′** and **4′** (Scheme 1). The equilibrium is considerably shifted towards the species **3** and **4**. In fact, the preferable binding of copper(II) into bridging cyanide is due to the high local concentration of the ligand. The tendency to form two dinuclear complexes with bridging cyanide persists even when **1** is dissolved in KCN-saturated CD_3OD. One of the pyrrole resonances of both **3** and **4** (designated by asterisks at Trace E) are broader than the remaining three, due to dipolar broadening from neighbouring Cu^{II} metal ion. Their concentration dependence of chemical shift is also larger. Those resonances belong probably to the 1-β-pyrrole protons located the closest to the Cu^{II} centre.

The minor species present in solution containing **1** and [TBA][CN] in chloroform solution requires a comment. The species **5** formed in the undertitrated solution was also found in case of titration of **2** with cyanide salts in chloroform solutions. The iron(III) centre is in high-spin electronic state as it can be concluded from the typical position of the pyrrole resonances in ^1H NMR spectrum (Trace C). It contains one cyanide ligand bound preferentially via carbon donor into iron(III). The magnetic non-equivalence of pyrrole resonances if compared to that of the starting high-spin complex as well as their larger bandwidth suggest that this can be caused by the proximity of a copper(II) centre. Therefore, the putative structure of **5** should be represented rather by that at Scheme 1 than any other.

The important question to answer seems to be the assignment of NMR β-pyrrole resonances and IR bands into the species **3** and **4**. At the early stage of titration (0.6 equivalents cyanide added, see Fig. 3) the bridging stretching vibration centred at 2212 cm^{-1} has got a higher intensity than that at 2185 cm^{-1}. The inspection of NMR spectrum at that titration level (Fig. 2, trace B) shows that species **3** and **4** have a comparable concentration. Moreover, the species **5** is present at a noticeable proportion and that one contributes to the intensity of IR band at 2212 cm^{-1}. At higher concentration of cyanide, (>1.5 equiv. added) the intensity of the IR band at 2185 cm^{-1} prevails due to higher concentration of species **3** and absence of species **5**. Therefore, the band at 2122 cm^{-1} is assigned into Fe^{III}–CN–Cu^{II} framework (species **5** and **4**) while that one at 2185 cm^{-1} is considered to originate from the cyanide-linkage isomer **3** with an Fe^{III}–NC–Cu^{II} fragment. The relationship between the cyanide bridging frequency and electronic structure of bridging metals observed here is rather general. It has been evidenced that if the cyanide C-bound centre (here it is Cu^{II} in **3**) is more electron-rich than the counterpart (Fe^{III} in **3**), this isomer has a lower ν(CN) frequency than the other one [55].

There is another minor species **6** observed in the ^{1}H NMR spectra, which reveals the largest ligand concentration/chemical shift dependence. At this stage of studies the origin of that spectrum can not be definitely specified. The hydroxide- or oxide- bridged species might be an explanation, because in those species the interporphyrin distance is shorter and electronic coupling between two metal ions is known to be substantially larger if compared with cyanide-bridged analogues. Moreover, the alkaline conditions used in the titration with [TBA][CN] would promote the formation of the form containing hydroxide anion. The attempts to isolate solid OH(Fe^{III}-*o*-O-$(CH_2)_2$-O-*o*-TTPCu^{II}) failed. The increase of concentration of solution of that complex always led to the formation of the intermolecular μ-oxo-(iron(III),copper(II) diporphyrin)$_2$ complex. The hydroxo complex is, however, the dominating form in dilute solutions. Besides, the intramolecularly oxo-bridged species is less probable due to highly negative 2- charge of putative **6**. Thus the preferred structure of **6** would be that presented at scheme 1 along with its adduct with the external cyanide **6′** and the equilibrium between those two complexes is responsible for cyanide concentration dependence of chemical shift of **6** observed in ^{1}H NMR spectra.

The absence of isosbestic points in UV–vis titration experiment is consistent with the complicated equilibria in the chloroform solutions containing **1** and [TBA][CN]. In comparison with the system containing symmetrical, diiron(III) complex **2** and [TBA][CN], the heterodinuclear Fe^{III}/Cu^{II} diporphyrin complex is involved in the additional equilibrium with weakly bound cyanide. The asymmetry of the heterodinuclear complex induces cyanide-linkage isomerism clearly demonstrated here by combined IR and ^{1}H NMR spectral methods. Whereas the Fe^{III}–CN–Cu^{II} bridging had been found before in many isolated and structurally characterized dinuclear Fe^{III}/Cu^{II} complexes containing iron(III)porphyrin [32–35], the bridging isomer with cyanide bound to iron(III)porphyrin centre *via* nitrogen has been identified for the first time in this study.

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