Synthesis of μ-Cyano(2,3-naphthalocyaninato)iron(III) and Comparison to μ-Cyano(phthalocyaninato)iron(III)

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Potassium dicyano(2,3-naphthalocyaninato)ferrate(III), K[2,3-NcFe(CN)$_2$] (2), reacts in water with elimination of KCN to form μ-cyano(2,3-naphthalocyaninato)iron(III), [2,3-NcFe(CN)]$_n$ (4a). Dichloro(2,3-naphthalocyaninato)iron(III), 2,3-NcFeCl$_2$ (3), reacts with KCN to yield also [2,3-NcFe(CN)]$_n$ (4b). Both compounds 4a and 4b show similar IR spectra with a typical blue-shifted CN valence frequency caused by a bridging function of CN$^-$. Compounds 4a and 4b also show almost identical ^{57}Fe-Mössbauer spectra which, however, might be interpreted with a Fe(+II) oxidation state of the iron. The measured magnetic moment of 4 however clearly proves the expected oxidation state +III of the iron in [2,3-NcFe(CN)]$_n$ (4). Compounds 4a and 4b both exhibit good semiconducting properties ($\sigma_{RT} \approx 10^{-3}$ S/cm) without additional external oxidative doping. The property is quite similar to that of the known μ-cyano(phthalocyaninato)iron [PcFe(CN)]$_n$ ($\sigma_{RT} \approx 10^{-2}$ S/cm).

The semiconducting properties of bisaxially coordinated macrocyclic bridged transition metal complexes [Mac-M(L)]$_n$ containing phthalocyanine (Pc), tetrabenzoporphyrin (TBP), or 1,2- and 2,3-naphthalocyanine (1,2-, 2,3-Nc) as the macrocycle (Mac), transition metals, e.g. iron or ruthenium in the oxidation state +II as the central metal atom (M), and ligands (L) like pyrazine (pyz), tetrazine (tz), diisocyanobenzene (dib) have been systematically investigated[1,2].

Another type of bridged systems contains the central transition metal atom e.g. Co, Rh, Fe, Mn, Cr in the oxidation state +III. Appropriate bridging ligands are negatively charged molecules as e.g. cyanide, thiocyanate, or azide. The displacement of an axial anion X$^-$ by bidendate CN$^-$, SCN$^-$, or N$_3^-$ (L$^-$) in a coordinatively unsaturated compound PcMX (X = Cl, OAc, CCl$_3$CO$_2$) provides a direct route to this type of coordination oligomers [PcM(L)]$_n$[3]. This route has been utilized for the synthesis of cyano complexes [PcM(CN)]$_n$ (M = Fe[4], Mn[5]), thiocyanato complexes [PcM(SCN)]$_n$ (M = Fe[6], Mn[7], Co[8]), and azido complexes [PcM(N$_3$)] (M = Cr[7], Mn[7]).

The starting materials PcFeCl[9] and PcMnCl[10] were prepared from the parent phthalocyanines PcFe and PcMn, respectively, by treating them with chlorinating agents, e.g. thionyl chloride. The chlorides and acetates PcMX (X = Cl, OAc, CCl$_3$CO$_2$) were converted into the bridged complexes [PcM(L)]$_n$ in aqueous or ethanolic alkali metal cyanide, thiocyanate, and azide solutions[4−8].

A convenient method for the introduction of the Pc^{2-}M^{3+} unit starting from the known dichloro derivatives PcCoCl$_2$[10] has been developed[5,11]. In these compounds the oxidation state of the macrocycles is assumed to be −I and of the metal +III. Again the starting compounds were converted into the oligomers in an aqueous alkali metal cyanide solution[4,5,12].

A general route leading also to cyano-bridged complexes [PcM(CN)]$_n$ is the elimination of alkali metal cyanide from alkali metal dicyano(phthalocyaninato)transition metallate-(III) complexes M′[PcM(CN)$_2$] (M′ = Na, K; M = Co[11], Rh[13], Fe[4], Mn[5], Cr[5]). The same method can be used for the preparation of [PcCo(SCN)]$_n$ from K[PcCo(SCN)$_2$][8].

The syntheses of the complexes M′[PcM(CN)$_2$] were possible either by in situ oxidation of PcM (M = Co, Mn) with atmospheric oxygen in the presence of an excess of cyanide or by reaction of the chloro compounds PcMCl$_2$ (M = Co, Cr) and PcMCl (M = Rh, Fe, Mn) with alkali metal cyanide[3,11]. The oligomers [PcM(CN)]$_n$ are formed by treatment of the mononuclear complexes M′[PcM(CN)$_2$] with water[11].

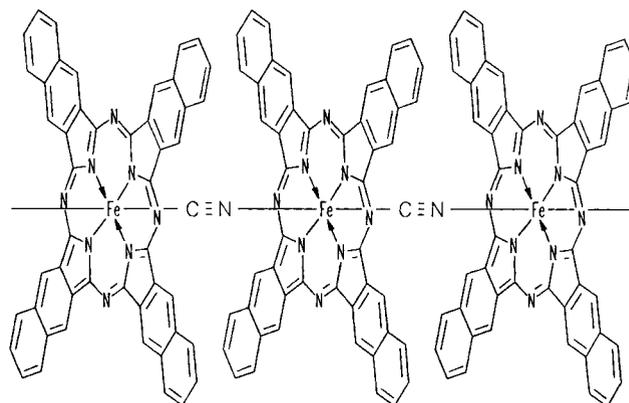Figure 1. Schematic structure of [2,3-NcFe(CN)]$_n$ (4)

The mononuclear complexes $M'[PcM(CN)_2]$ ($M' = Na$, K; $M = Co$, Rh, Fe, Mn, Cr) were characterized by IR, FIR, UV/Vis and in some cases by ^{1}H-NMR spectroscopy[5,11,13,14]. The IR data exhibit CN valence frequencies around 2130 cm^{-1}, which are in the anticipated region for terminal Co^{3+}, Cr^{3+}, and Rh^{3+} cyano groups[15].

The CN valence frequencies of the bridged compounds are shifted to higher energy by about 20 cm^{-1} as compared with the mononuclear complexes $M'[PcM(CN)_2]$. This increase in CN valence frequencies is a good indication for the presence of a cyano bridge in $[PcM(CN)]_n$[3,16].

A pentacoordinated PcCoCN, which differs in its spectral properties from $[PcCo(CN)]_n$, was obtained electrochemically from $K[PcCo(CN)_2]$[17].

The complexes $[PcM(CN)]_n$ exhibit comparatively high electrical conductivities between 10^{-3} and 10^{-2} S/cm without additional external doping. $[PcCo(CN)]_n$ shows also a good photoconductivity[18].

In this paper we report on the synthesis and characterization of the cyano-bridged system $[MacFe(CN)]_n$, in which the macrocycle is 2,3-naphthalocyanine, 2,3-Nc (1) (see Figure 1).

Results and Discussion

For the synthesis of $[2,3-NcFe(CN)]_n$ (4) (2,3-naphthalocyaninato)iron(II), 2,3-NcFe (1), was required. 2,3-NcFe (1) was already prepared in 1969 from 2,3-dicyanonaphthalene, iron dust, and ammonium molybdate[19]. Our earlier attempts to reproduce this reaction yielded only insufficiently pure products[20,21]. Complex 1 was prepared more easily by the reaction of 2,3-dicyanonaphthalene with pentacarbonyliron[21,22] (see Scheme 1).

Scheme 1. Synthesis of 2,3-NcFe (1)
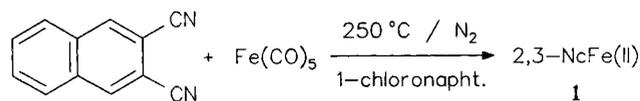
Although 2,3-NcFe (1) was not stored in an inert atmosphere the IR spectrum showed even no changes after some months and was identical with the spectrum reported earlier[21]. From the elemental analytical data, which differ from the calculated ones, we cannot exclude some oxygen or other inorganic impurities in the product. On the other hand it is often observed that phthalocyaninato compounds show poor elemental analytical data[23]. Possible oxidated products are expected, if we consider that the oxidation potential of 1 (E[Fe(II)/Fe(III)] = 0.43 V vs. SCE) is 0.15 V lower than that of (phthalocyaninato)iron, PcFe[2d]. During the preparation of (phthalocyaninato)iron compounds often μ-oxo dimers such as $(PcFe)_2O$ are formed, which may occur in two isomeric structures, one with a bent Fe—O—Fe moiety [μ-oxo (1)] and another one with a linear or quasi-linear Fe—O—Fe moiety [μ-oxo (2)], which can be detected and distinguished by Mössbauer spectroscopy. The quadrupole splitting ΔE_Q of μ-oxo (2) was found to be at most 1.28 mm/

s and that of μ-oxo (1) to be 0.42 mm/s[24]. 2,3-NcFe (1) only has one doublet ($\delta = 0.36$ mm/s, $\Delta E_Q = 2.21$ mm/s at room temperature), which can be assigned to 1. μ-Oxo dimers therefore can be excluded as impurities in our product.

The electronic spectrum of 2,3-NcFe (1) in pyridine, where $2,3-NcFe(py)_2$ is formed, shows a good resolution with the Q band at $\lambda_{max} = 755$ nm, 100 nm red-shifted related to PcFe in pyridine. This is not surprising, because the linear annulated benzene rings in 1 exhibit an extended mesomeric π system[25].

As mentioned above there are at least two methods for the preparation of cyano-bridged macrocyclic metal complexes. Thorough investigations of the synthesis of $[PcFe(CN)]_n$ were made by us already some time ago[4,26,27]. Identical products were obtained by the reaction of PcFe and potassium cyanide in water, bubbling air into the suspension as well as by replacing the chlorine in PcFeCl by cyanide. In the first route $K_2[PcFe(CN)_2]$ was formed as an intermediate[4,26], visible by the green color of the solution. Subsequent oxidation by atmospheric oxygen leads to $[PcFe^{3+}-(CN)]_n$[4,26]. Earlier reports on the synthesis of bisaxially coordinated compounds $M'[PcFe^{3+}(CN)_2]$, where $M' = PNP$ (= bistriphenylphosphiniminium) or TBA (= tetrabutylammonium), are known[28]. In the present work the complexes are formed by replacing axial ligands such as OH^- and Cl^- in $PNP[PcFe(OH)_2]$ and PcFeCl by CN^-. In the case of the biscyano complexes $M'[PcFe^{3+}(CN)_2]$ a CN valence frequency was not observed in the IR spectra[28]. Obviously, the influence of the cation on the IR spectra must be taken into account. The preparation of PcFeCN by the reaction of $TDBA[PcFe(CN)_2]$ (TDBA = tridodecylbutylammonium) with iodine is also described, but this compound has only been characterized by an elemental analysis[28].

We used the synthetic pathways reported by us earlier[4,26] to obtain $[2,3-NcFe(CN)]_n$ (4). On the one hand, we splitted off one ligand from the monomer $K[2,3-NcFe(CN)_2]$ (2), denoted as method a). On the other hand, we replaced the chloro ligands in the monomer $2,3-NcFeCl_2$ (3) by cyanide (method b) (see Scheme 2). In both cases, we obtained mainly the same product.

Scheme 2. Synthesis of $[2,3-NcFe(CN)]_n$ (4) according to methods a) and b)
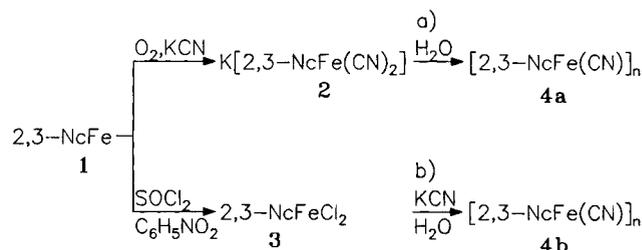
With method a) air was bubbled into a suspension of 2,3-NcFe (1) and potassium cyanide in ethanol. After filtration the solid material was extracted with acetone. The isolated product was assumed to be a bisaxially coordinated complex $K[2,3-NcFe(CN)_2]$ (2). We could only obtain an IR and an UV/Vis spectrum, because the product was contaminated

with excess cyanide. A pure product without this impurity decomposes. The IR spectrum exhibits two absorptions at 2090 and 2073 cm^{-1}. The first absorption can be assigned to excess potassium cyanide, the second one is attributed to the CN valence vibration of the cyanide ligand in **2**. The CN frequency is strongly influenced by the oxidation state of the coordinated metal atom[29]. Compared with K[PcFe^{3+}(CN)$_2$] ($\tilde{v}$ = 2112 cm^{-1})[4] and K$_2$[PcFe^{2+}(CN)$_2$] ($\tilde{v}$ = 2065 cm^{-1})[4] we should assume Fe(+II) rather than Fe(+III) in our product **2**. But as PcFe is oxidized under the same conditions as 2,3-NcFe (**1**) and is more stable towards oxidation than **1** we suggest the oxidation state +III for Fe in **2**. Elucidation of the structure by an X-ray analysis has not yet been possible.

In the UV/Vis spectrum of **2** recorded in ethanol the Q band appears at λ_{max} = 748 nm which is only few nanometers blue-shifted relatively to that of 2,3-NcFe (**1**) in pyridine, present as 2,3-NcFe(py)$_2$.

To prepare the cyano-bridged compound [2,3-NcFe(CN)]$_n$ (**4a**), K[2,3-NcFe(CN)$_2$] (**2**) was boiled for three days in water, filtered off and thoroughly washed with water.

Method b) starts with the dichloro adduct 2,3-NcFeCl$_2$ (**3**). The preparation of PcMCl$_2$ (M = Co, Fe, Cr) by oxidation of PcM with thionyl chloride in nitrobenzene is described in ref.[10] Because of the lower oxidation potential of 2,3-NcFe (**1**) compared to that of PcFe (see above) we could use more gentle conditions for this reaction. A suspension of freshly distilled nitrobenzene, **1**, and freshly distilled thionyl chloride was stirred at room temperature and not at 60 to 70 °C as reported for the preparation of PcMCl$_2$[10]. If the temperature was raised up to 60 °C our product contained 10.7% chlorine. Excess chlorine was not changed even after the reaction of the chlorinated product with sodium cyanide in water (see below), which leads to the conclusion, that at the elevated temperatures the macrocycle is chlorinated.

The IR spectrum of 2,3-NcFeCl$_2$ (**3**) is mainly identical with the spectrum of a sample, which was prepared earlier[21], but it is quite different from that of 2,3-NcFe (**1**)[21]. The intensities of many peaks in the finger-print area are diminished. This fact, which is already known from Pc(−I)Fe(III)Cl$_2$[10] was explained by a delocalization of the radical electron causing increasing equivalence of the bonds.

In the mass spectrum of 2,3-NcFeCl$_2$ (**3**) only a peak at m/z = 804 (2,3-NcFeCl$^+$) and one at 768 (2,3-NcFe$^+$) was found, although we used the FAB method.

The whole mass loss of **3** in TG/DTA was 14% (calculated 8.5% for the loss of two Cl) beginning at about 120 °C. The unexpectedly high mass loss shows the comparatively low stability of the macrocycle.

The UV/Vis spectrum of **3** recorded in pyridine exhibits the same position for the Q band as 2,3-NcFe (**1**) in pyridine at λ_{max} = 755 nm. So both compounds are present as 2,3-NcFe(py)$_2$. As expected, the axially coordinated chlorine in **3** has been replaced by pyridine with reduction of the iron from +III to +II.

The ^{57}Fe-Mössbauer spectrum of 2,3-NcFeCl$_2$ (**3**) confirms the axial positions of the chloro ligands. A comparison with PcFe(III)Cl$_2$ (δ = 0.35 mm/s, ΔE_Q = 2.15 mm/s) is not pos-

sible due to the fact that no reference compound and no temperature were given[10]. The isomer shift δ = 0.18 mm/s and the quadrupole splitting ΔE_Q = 2.47 mm/s at room temperature are quite similar to the corresponding values of PcFe(III)Cl (δ = 0.20 mm/s, ΔE_Q = 2.62 mm/s[30,31]). The influence of the different macrocycles can be neglected as has been shown in other cases[31]. Therefore, we assign the oxidation state +III to the central iron in **3**, because it mainly influences the isomer shift. This fact excludes another position of the chlorine, e.g. in the macrocycle 2,3-Nc.

[2,3-NcFe(CN)]$_n$ (**4b**) could now be obtained by heating a suspension of 2,3-NcFeCl$_2$ (**3**) in a solution of sodium cyanide in water for three days. The product was filtered off and extracted with acetone.

The spectral properties of [2,3-NcFe(CN)]$_n$ (**4**) prepared by method a) (**4a**) compared to that by method b) (**4b**) are as follows:

The IR spectra of both products are almost equivalent, showing a sharp absorption at $\tilde{v}$ = 2087 cm^{-1} which is assigned to the CN valence vibration. It is blue-shifted by 14 cm^{-1} compared to that of K[2,3-NcFe(CN)$_2$] (**2**) ($\tilde{v}$ = 2073 cm^{-1}, see above). A blue-shifted CN valence frequency is normally caused by a bridging function of CN$^-$ as known from many examples, e.g. [PcCo(CN)]$_n$ ($\tilde{v}$ = 2158 cm^{-1}) vs. Na[PcCo(CN)$_2$] · 5 H$_2$O ($\tilde{v}$ = 2130 cm^{-1})[11] or CuCN (Cu—CN—Cu bonding, $\tilde{v}$ = 2172 cm^{-1}) vs. K[Cu(CN)$_2$] (Cu—CN bonding, $\tilde{v}$ = 2125 cm^{-1})[32]. But compared with [PcFe^{3+}(CN)]$_n$ ($\tilde{v}$ = 2133 cm^{-1}) vs. [HPcFe^{2+}(CN)]$_n$ ($\tilde{v}$ = 2065 cm^{-1})[4] one should rather assume Fe(+II) than Fe(+III) in **4**.

The ^{57}Fe-Mössbauer spectrum of **4b** at room temperature is given in Figure 2. Both compounds **4a** and **4b** have an almost identical spectrum with an isomer shift δ = 0.18 mm/s and almost the same quadrupole splitting ΔE_Q = 1.67 mm/s (**4a**) and 1.62 mm/s (**4b**). From a comparison of these results with the Mössbauer spectra of [PcFe^{3+}(CN)]$_n$ (δ = 0.09 mm/s, ΔE_Q = 1.94 mm/s at 294 K[31,33]) and [HPcFe^{2+}(CN)]$_n$ (δ = 0.28 mm/s, ΔE_Q = 1.47 mm/s at 77 K[31,34]) we may infer that the iron in **4** has the oxidation state +II rather than +III.

The measured magnetic moment of **4b** shows a temperature dependence (μ_{eff} = 0.9 B.M. at 10 K to 2.5 B.M. at 310 K). The diamagnetic correction (−480 · 10^{-6} emu/mol) was
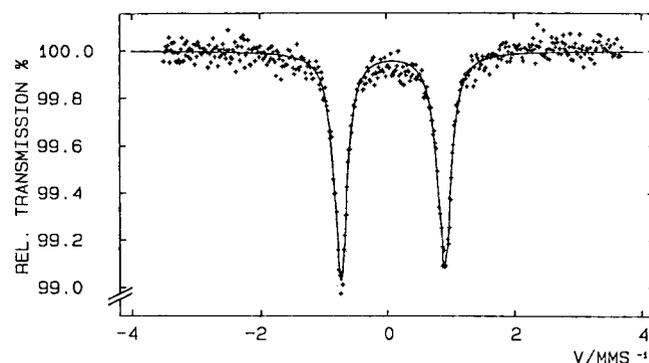

Figure 2. ^{57}Fe-Mössbauer spectrum of [2,3-NcFe(CN)]$_n$ (**4b**)

calculated by the method of Haberditzl[35] and from a magnetic measurement of PcH$_2$ ($-307 \cdot 10^6$ emu/mol)[36]. A comparison with the magnetic moment of [PcFe(CN)]$_n$[4,26] ($\mu_{eff} = 2.4$ B.M. at 293 K) clearly indicates the oxidation state +III for the iron atom (d^5 low-spin ion, S = $\frac{1}{2}$, $\mu_{s.o.} = 1.7$ B.M.) in 4b. On the other hand, [PcFe(CN)]$_n$ does not show a temperature dependence of the magnetic moment ($\mu_{eff} = 2.2$ B.M. at 93 K). Perhaps antiferromagnetism and spin-orbital coupling are responsible for the temperature-dependent magnetic measurement of 4b. It is already known that [PcCr(F)]$_n$ is antiferromagnetic and [PcCr(CN)]$_n$ ferromagnetic, but these facts are supported by extensive calculations and measurements down to 4 K, so that a comparison with these compounds is difficult[37].

If we accept an oligomeric structure for 4 as, in principle, supposed for [PcFe(CN)]$_n$ (see Figure 1)[3], some reflections on the electronic configuration of 4 may nevertheless adjust the Mössbauer results to the oxidation state +III of the iron atom[38]. If we describe the electronic configuration of 4 by means of the same MO scheme as calculated for PcFe we obtain for Fe(+III) in 4 (d$_{xy}$)^2 (d$_{xz}$, d$_{yz}$)^3 or (d^{2}sp^3)^5[39], whereas CN$^-$ has the configuration $(\sigma_s^b)^2(\sigma_s^*)^2(\pi_{x,y}^b)^4(\sigma_z^b)^2(\pi_{x,y}^*)^0$[37]. The isomer shift depends on the electron density at the nucleus and therefore is mostly influenced by the occupation of the s orbitals. The higher the electron density at the nucleus, the more negative is the isomer shift. So we suggest a weaker σ donor bond from CN$^-$ to Fe [$(\sigma_z^b)^2 \rightarrow$ (d^{2}sp^3)^5] than in [PcFe(CN)]$_n$, because the influence of the s orbital is more important than that of the screening effect of the d orbitals. Furthermore we suggest a weaker π acceptor bond to the ligand [(d$_{xz}$, d$_{yz}$)^3 $\rightarrow$ ($\pi_{x,y}^*$)^0] compared with [PcFe(CN)]$_n$, whereas the bonding conditions are more influenced by the π acceptor bond than by the σ donor bond. This assumption is consistent with the lower valence frequency of the CN bond of [2,3-NcFe(CN)]$_n$ (4) ($\tilde{v} = 2087$ cm^{-1}) relative to [PcFe(CN)]$_n$ ($\tilde{v} = 2133$ cm^{-1}). The weaker bond between the ligand CN$^-$ and the metal atom Fe (CFe and/or NFe bond) compared with [PcFe(CN)]$_n$ may be caused by a stronger repulsion of the larger macrocycle 2,3-Nc. So we also assume a larger distance between two macrocycles within the chain of [2,3-NcFe(CN)]$_n$ than of [PcFe(CN)]$_n$. But this could only be confirmed by a single-crystal X-ray investigation.

We are not sure about the purity of 4a: the elemental analysis of 4a is not consistent with a formula [2,3-Nc-Fe(CN)]$_n$ but with [2,3-NcFe(CN)]$_n \cdot$ 3 H$_2$O. On the other hand, oxygen was introduced during the formation of the monomer K[2,3-NcFe(CN)$_2$] (2) when air was bubbled through the suspension. The Mössbauer spectrum of 4a shows a second doublet of low intensity at $\delta = 0.33$ mm/s and $\Delta E_Q = 0.76$ mm/s which can be assigned to small amounts of μ-oxo (1) impurities (see above). The elemental analytical data of 4b deviate from the calculated values. However, we have not been able so far to identify the impurity. But as mentioned above, the elemental analytical data of phthalocyaninato compounds are often not satisfying[23]. Maybe they are not completely burned during the analysis.

Results of conductivity measurements of pressed pellets of 4 are given in Table 1 together with those of related compounds. The measurements were performed at room temperature and at 10^8 Pa pressure by using the van der Pauw four-probe method[40]. The conductivities of pressed pellets can differ strongly, because they are dependent on grain size and grain boundary resistance. Otherwise, they agree with microwave conductivity measurements, which do not need contact to the samples[41]. The cyano-bridged compounds listed in Table 1 show good semiconducting properties without additional external oxidative doping. The reason for these comparatively high conductivities is not completely understood yet. According to calculations a conductivity mechanism based on a band structure has been suggested[42,43].

Table 1. Conductivities of [2,3-NcFe(CN)]$_n$ (4) and selected cyano-bridged (phthalocyaninato)metal complexes

Compound	cond. σ (S/cm)	ref.
[2,3-NcFe(CN)]$_n$ (4a)	$1 \cdot 10^{-3}$[b]	this work
(4b)	$1 \cdot 10^{-4}$[b]	this work
[PcFe(CN)]$_n$	$6 \cdot 10^{-3}$[b]	[4]
[PcCo(CN)]$_n$	$2 \cdot 10^{-2}$[b]	[11]
[PcCr(CN)]$_n$	$3 \cdot 10^{-6}$[a]	[5]
[PcMn(CN)]$_n$	$1 \cdot 10^{-5}$[b]	[5]
[PcRh(CN)]$_n$	$4 \cdot 10^{-4}$[b]	[13]
[HPcFe(CN)]$_n$	$8 \cdot 10^{-4}$[b]	[4]

[a] Two-probe technique. — [b] Four-probe technique.

Experimental

FT-IR: Bruker IFS 48. — UV/Vis: Shimadzu UV-365. — TG/DTA: Netzsch-Simultan-STA 409. — MS: Varian Mat 711 (FAB). — ^{57}Fe-Mössbauer spectra: Elscint AME-30, constant acceleration mode, ^{57}Co/Rh, Fe as reference. — Magnetic measurement: Squid Magnetometer, MPMS system. — Elemental analyses: Carlo Erba Elemental Analyser 1104, 1106.

2,3-Dicyanonapthalene was prepared according to ref.[44] The solvents were purified according to known procedures.

(2,3-Naphthalocyaninato)iron(II), 2,3-NcFe (1)[21]: To a solution of 2,3-dicyanonaphthalene (5.34 g, 0.03 mol) in 1-chloronaphthalene (20 ml) was added at 250°C a solution of Fe(CO)$_5$ (2.12 g, 0.01 mol) in 1-chloronaphthalene (10 ml) during 45 min. The mixture was then stirred at 250°C for 1 h, then cooled and filtered. The residue was washed several times with chloroform, toluene, and acetone. The crude product was refluxed for 10 min in 1 N HCl (50 ml) and subsequently in 1 N NaOH (50 ml), filtered and washed with water. Extraction with acetone afforded 4.6 g (79%) of the title compound as a green powder. — C$_{48}$H$_{24}$FeN$_8$ (768.7): calcd. C 74.99, H 3.15, N 14.58; found C 73.62, H 3.29, N 13.91.

Potassium Dicyano(2,3-naphthalocyaninato)ferrate(III), K[2,3-NcFe(CN)$_2$] (2): Air was bubbled through a suspension of 2,3-NcFe

(1) (0.77 g, 1.0 mmol) and potassium cyanide (1.30 g, 20 mmol) in 60 ml of ethanol for 3 d at 50°C. After filtration the solid residue was washed with 20 ml of ethanol. **2** was separated from unreacted **1** by Soxhlet extraction with acetone. − IR (KBr): $\tilde{v}$ = 2073 cm^{-1} (CN). − UV/Vis (ethanol): λ_{max} = 748 nm.

Dichloro(2,3-naphthalocyaninato)iron(III), 2,3-NcFeCl₂ (**3**): 2,3-NcFe (**1**) (1.0 g, 1.3 mmol) was suspended in a solution of thionyl chloride (1.5 ml, 2 mmol) in 15 ml of nitrobenzene. The suspension was stirred at room temp. for 3 h. The black solid was filtered and washed with ethanol and ether to yield 0.89 g (82%) of **3**. − IR (KBr): $\tilde{v}$ = 3055 cm^{-1}, 1597, 1514, 1468, 1447, 1342, 1263, 1200, 1148, 1128, 1086, 1045, 1020, 957, 897, 860, 854, 768, 747, 710. − MS (FAB), m/z (%): 804 (2) [M$^+$ − Cl], 768 (43) [M$^+$ − Cl₂]. − ^{57}Fe-Mössbauer spectrum: δ = 0.18 mm/s (293 K), 0.25 (82 K), ΔE_Q = 2.47 mm/s (293 K), 2.47 (82 K). − C₄₈H₂₄Cl₂FeN₈ (839.6): calcd. C 68.66, H 2.88, Cl 8.45, N 13.35; found C 65.76, H 2.97, Cl 8.32, N 12.58.

μ-Cyano(2,3-naphthalocyaninato)iron(III), [2,3-NcFe(CN)]ₙ (**4**): *Procedure a)* **4a** was prepared by boiling **2** in water for 3 d. The solid product was filtered and thoroughly washed with water. − *Procedure b)* **3** (0.84 g, 1.0 mmol) and potassium cyanide (0.98 g, 15 mmol) were suspended in 50 ml of water. The mixture was refluxed for 3 d, filtered and washed with water. Extraction with acetone completed the purification yielding 0.66 g (85%) of a dark green powder. − IR (KBr): $\tilde{v}$ = 2087 cm^{-1} (CN). − ^{57}Fe-Mössbauer spectrum (293 K): δ = 0.18 mm/s, ΔE_Q = 1.67 mm/s (**4a**), 1.62 (**4b**). − TG (**4b**) (dissociation range, mass decrease): 190−290°C, 4.2%. − Magnetic measurement (**4b**): μ_{eff} = 0.9−2.5 B.M. (10−310 K). − Conductivity measurement: 10^{-3} S/cm (**4a**), 10^{-4} (**4b**) (293 K, 10^8 Pa). − C₄₉H₃₀FeN₉O₃ (848.7) (according to procedure a): calcd. C 69.33, H 3.53, Fe 6.60, K 0.00, N 14.85, O 5.66; found C 69.73, H 3.34, Fe 6.28, K 0.13, N 15.27, O 5.65. − C₄₉H₂₄FeN₉ (794.7) (according to procedure b): calcd. C 74.06, H 3.04, Cl 0.00, N 14.86; found C 68.11, H 3.24, Cl 0.07, N 14.52.

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