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BISAXIALLY COORDINATED MACROCYCLIC TRANSITION METAL COMPLEXES

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CONTENTS

A. INTRODUCTION

Metallomacrocycles, like metallophthalocyanines and tetrabenzoporphyrines, besides their many other possible applications as, e.g., dyes, pigments, catalysts, etc., have recently been investigated most intensively with respect to their electrical properties. Metallophthalocyanines and, e.g., metallotetrabenzoporphyrines, have been investigated mainly as part of efforts to construct new types of low-dimensional compounds [1]. In these the metallomacrocycles achieve a stacked cofacial arrangement with a suitable low interplanar distance to allow electron delocalization by $\pi-\pi$ overlap. After partial oxidation or reduction (doping) of the macrocycles, good conducting or semiconducting properties of such compounds have been observed [1].

One method for the construction of stacked metallophthalocyanines and tetrabenzoporphyrines is the so-called "shish kebab" approach [1] in which the metallomacrocycles are linked together by bisaxially metal bonded bridging ligands. A schematic drawing of this type of bridged macrocyclic metal compound $[\mathrm{MacML}]_n$ (MacM = PcM, TBPM, etc.) is given in Fig. 1. The synthesis of such polymers, using bridging ligands L of differing lengths, allows a systematic variation of the distance of the cofacial macrocycles and thereby controls the electrical properties of these compounds.

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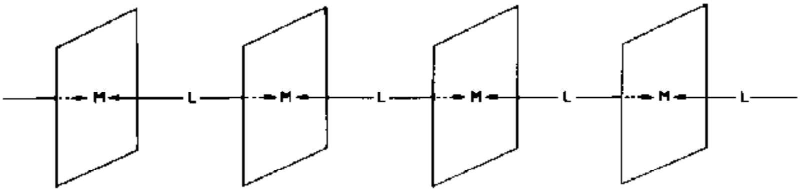


Fig. 1. Bridged macrocyclic transition metal polymers: M = metallomacrocycle; L = bidentate bridging ligand.

Bridged macrocyclic metal compounds, of the structure shown in Fig. 1, with transition metals (Fe, Ru, Co, Rh...), which prefer an octahedral configuration of the ligands, have been synthesized by Hanack et al. [1]. The bridging ligands are organic molecules containing delocalizable π-electrons, e.g., pyrazine (pyz), cyanide (CN^-), thiocyanate (SCN^-) or $C{\equiv}C^{2-}$. By using these combinations of transition metal phthalocyanine- or tetrabenzoporphyrine and a π-electron containing bridging ligand, the corresponding polymers often show semiconducting properties even without external oxidative doping. Interesting magnetic properties, non-linear optic properties and photoconductivity are also observed in some of these compounds.

The bridging ligand L in the compounds shown in Fig. 1 can be linked to the central metal atom of the macrocycles in three different ways, e.g., with two coordinated bonds as in the case of pyz, by one σ- and one coordinate bond, e.g. with CN^-, or by two σ-bonds, e.g., with $C{\equiv}C^{2-}$.

Part of our work has concentrated on the synthesis and characterization of the first type of bridged macrocyclic metal compounds with two coordinated bonds of a bidentate ligand L to the central transition metal. Suitable bridging ligands L for this type of bonding are, e.g. pyz, bipyridine (bpy), 1,4-diisocyanobenzene (dib), 1,2,4,5-tetrazine (tz), etc.

In the following review these type of compounds and the corresponding bisaxially substituted monomers $MacML_2$ (Mac = Pc, TBP...; M = Fe, Ru, Co...; L = pyz, bpy, dib, tz....) will be discussed. For the other types see the literature [1].

B. SYNTHESIS AND CHARACTERIZATION OF COMPLEXES WITH PYRAZINE, SUBSTITUTED PYRAZINES, 1,2,4,5-TETRAZINE AND 1,4-DIAZABICYCLO[2.2.2]OCTANE AS AXIAL LIGANDS

For the construction of an arrangement of metallomacrocycles shown in Fig. 1 with linear π-electron-containing bidentate ligands L, we first used phthalocyaninatoiron (PcFe) as the macrocycle and pyz (see Fig. 2) as the bridging ligand L. PcFe easily reacts with monodentate aliphatic and aromatic nitrogenous bases [2–12], phosphines and phosphites [13], isocyanides [2,13,14] and other C-, N-, S- or O-donor ligands L [15–19] to form

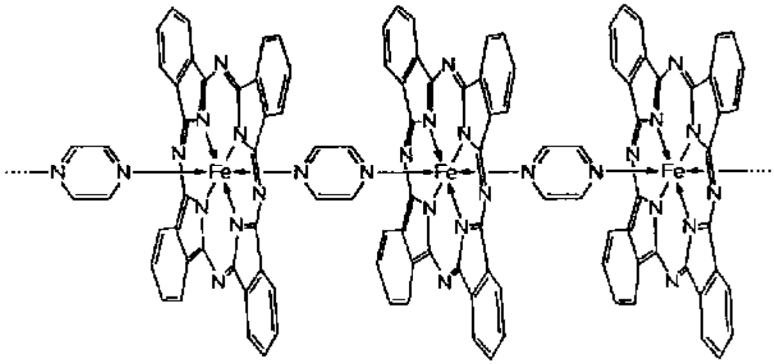


Fig. 2. Schematic drawing of phthalocyaninato(μ-pyrazine)iron(II).

monomeric $PcFeL_2$ adducts. The axial coordination of the ligands perpendicular to the plane of the macrocycle has been confirmed via X-ray diffraction studies of such complexes [20–22].

For more detailed information about the coordination behaviour of pyrazine, a new series of $PcFeL_2$ adducts with L = pyz, 2-methylpyrazine (mepyz), 2,6-dimethylpyrazine (me_2pyz), 2-ethylpyrazine (etpyz) and 2-chloropyrazine (Clpyz) were synthesized from PcFe by reacting it with the pure liquid ligand at elevated temperatures [23]. Ligand exchange reactions are unsuitable for the preparation of $PcFeL_2$ adducts as monomeric PcFe bis-adducts with two different ligands PcFeLL′ are formed [13]. The pyrazines can act both as monodentate and bidentate ligands: $PcFeL_2$ adducts

TABLE 1

TG/DTA data of monomeric $PcML_2$ and polymeric $[PcM(pyz)]_n$ (M = Fe, Ru) base adducts [a]

Compound	Dissociation range of base by TG (° C)	Mass loss (%)		$T_{max.}$ (endothermic) from DTA signal (° C)	Ref.
		Calc.	Found		
$PcFe(pyz)_2$	160–245	22.0	21.6	240	23
$PcFe(mepyz)_2$	170–230	24.9	24.4	225	23
$PcFe(me_2pyz)_2$	170–245	27.6	27.2	240	23
$PcFe(etpyz)_2$	145–215	27.6	26.6	210	23
$PcFe(Clpyz)_2$	145–200	28.7	27.7	195	23
$[PcFe(pyz)]_n$	240–310	12.4	12.5	295	23
$PcRu(pyz)_2$ [b]	255–305/330–560	20.7	20.0	285/540	24
$[PcRu(pyz)]_n$	330–560	11.5	10.9	540	24

[a] Simultaneous TG/DTA measurement under nitrogen (20 ml min^{-1}), heating rate 2 K min^{-1}.

[b] The base molecules are split off in two well resolved steps.

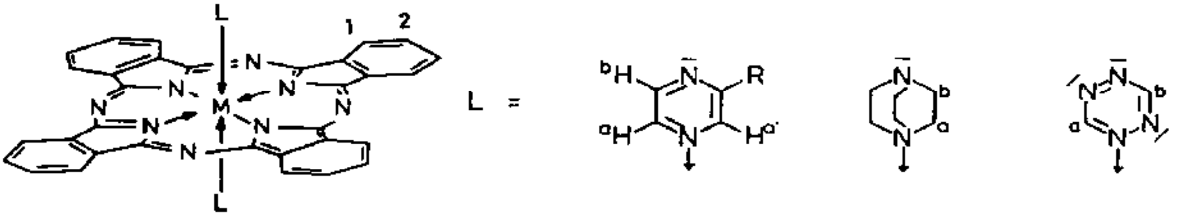
(with hexacoordinated iron), PcFeL (with pentacoordinated iron), dimeric PcFe–L–FePc and polymeric $[PcFeL]_n$ are possible products. The prepared materials were examined, for their purity and for their stoichiometry, by using both combined thermogravimetric and differential thermal analysis (TG/DTA). Due to the thermal stability of PcFe in the absence of air the base adducts can be thermally decomposed to form defined products.

The results of the TG/DTA measurements show that all adducts have a PcFe : L ratio of 1 : 2. The TG/DTA data of some $PcFeL_2$ complexes are shown in Table 1.

$PcFeL_2$ adducts, in which L is a substituted pyrazine, are sufficiently soluble, e.g. in $CDCl_3$. Therefore these complexes can be investigated by ^1H

TABLE 2

^1H NMR Spectroscopic data of $PcML_2$ adducts with M = Fe, Ru and L = pyz, substituted pyrazines, 1,2,4,5-tetrazine and dabco [24,25,27] [a]



Compound	H [a]	H [b]	H [a']	R	H^1; H^2
$PcRu(pyz)_2$	2.35 [4]*m*(3)	6.43 [4]*m*(3)			9.20; 7.90 [8]; [8]
$PcRu(mepyz)_2$	2.15 [2]*d*(3)	6.30 [2]*d*(3)	2.17 [2]*s*	1.09 [6]*s*	9.19; 7.93 [8]; [8]
$PcFe(mepyz)_2$	1.92 [2]*d*(3)	6.01 [2]*d*(3)	1.94 [2]*s*	0.95 [6]*s*	9.35; 8.00 [8]; [8]
$PcRu(etpyz)_2$	2.20 [2]*d*(3)	6.29 [2]*d*(3)	2.17 [2]*s*	1.35 [4]*q*(7.5) 0.13 [6]*t*(7.5)	9.20; 7.93 [8]; [8]
$PcFe(etpyz)_2$	1.96 [2]*d*(3)	6.03 [2]*d*(3)	1.94 [2]*s*	1.23 [4]*q*(7.5) 0.03 [6]*t*(7.5)	9.35; 8.00 [8]; [8]
$PcRu(dabco)_2$	−2.43 [12]*t*(7.35)	0.68 [12]*t*(7.35)			9.16; 7.91 [8]; [8]
$PcRu(tz)_2$	3.79 [2]*d*(2.64)	7.69 [2]*d*(2.64)			9.29; 8.04 [8]; [8]

[a] Chemical shifts in ppm with $CDCl_3$ (7.24) as internal standard.

[b] Coupling constants (Hz) are in parentheses and the number of protons is given in brackets.

TABLE 3

^{57}Fe-Mössbauer data for iron(II)phthalocyanines and 2,3-naphthalocyanines with pyrazine, substituted pyrazines, 4,4′-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene, 1,2-bis(4-pyridyl)ethane, 4,4′-trimethylene bipyridine and tetrazine as axial ligands ($T = 298$ K).

Complex	δ (mm s^{-1}) [a]	ΔE_Q (mm s^{-1}) [a]	Ref.
PcFe	0.634 [b]	2.581	29
2,3-NcFe	0.36 [c]	2.21	30
PcFe(py)$_2$	0.26 [c]	2.02	4
PcFe(pyz)$_2$	0.500 [b]	2.006	31
[PcFe(pyz)$\cdot$0.5 C_6H_6]$_n$	0.500 [b]	2.009	31
[PcFe(pyz)]$_n$	0.18 [c]	1.98	32
[PcFe(bpe)]$_n$	0.20 [c]	2.01	32
[PcFe(bpy)]$_n$	0.24 [c]	2.00	32
[PcFe(bpa)]$_n$	0.28 [c]	2.04	32
[PcFe(tmbpy)]$_n$	0.28 [c]	2.06	32
PcFe(mepyz)$_2$	0.498 [b]	1.895	33
PcFe(me$_2$pyz)$_2$	0.498 [b]	1.968	33
PcFe(Clpyz)$_2$	0.513 [b]	2.149	33
PcFe(etpyz)$_2$	0.504 [b]	2.016	33
PcFe(tz)$_2$	0.15 [c]	1.79 [d]	30
[PcFe(tz)]$_n$	0.13 [c]	2.23	30
[2,3-NcFe(tz)$\cdot$0.5 CHCl$_3$]$_n$	0.19 [c]	1.97	30

[a] Fit to a quadrupole doublet.
[b] Relative to sodium nitroprusside.
[c] Relative to metallic iron.
[d] Additional doublet of PcFe.

NMR spectroscopy (see Table 2) [25]. The phthalocyaninato-ring protons appear as an AA′BB′ pattern at low field [26], whereas the Pc-ring current shifts the proton signals of the axial coordinated pyrazines to higher fields with respect to the non-coordinated ligands. The ^{1}H NMR spectra show that only the sterically unhindered nitrogen atom of the substituted pyrazine coordinates to the central iron atom in PcFe. All substituents (methyl-, ethyl-, chloro-) block the adjacent nitrogen atom. Therefore neither 2,5-dimethyl- nor 2,3,5,6-tetramethylpyrazine react with PcFe to form the appropriate PcFeL$_2$ adduct [23].

A suitable method for investigations in solid iron-containing compounds is ^{57}Fe Mössbauer spectroscopy. The most important Mössbauer parameters in chemical investigations are the isomer shift δ and the quadrupole splitting ΔE_Q [28] which facilitate conclusions about the oxidation state and the spin state of the iron nuclei and the arrangement of the ligands. Table 3 summarizes the Mössbauer data for some of the synthesized complexes. Both isomer shifts and quadrupole splittings are lowered with respect to

PcFe and are comparable to values reported for $PcFeL_2$ with L = substituted pyridines [11]. They confirm the low spin octahedral Fe(II) environment.

Due to steric hindrance, substituted pyrazines cannot be used as bidentate ligands to synthesize polymeric compounds. $[PcFe(pyz)]_n$ however is easily obtained by suspending PcFe in a boiling solution of pyz in chlorobenzene. In addition the monomeric $PcFe(pyz)_2$ readily splits off pyz in solvents like chloroform, benzene or chlorobenzene to form $[PcFe(pyz)]_n$ [23]. This reaction can be followed by UV/VIS spectroscopy. In the solvent used, e.g., benzene or chlorobenzene it was possible to record the spectrum of $PcFe(pyz)_2$ only in the presence of a 10^6 fold excess of pyz. Without excess of pyz, absorption occurs at about 700 and 780 nm and increases in intensity, due to the formation of the bridged $[PcFe(pyz)]_n$. The strongest transitions of $[PcFe(pyz)]_n$ occur at 788, 723 and 714 nm, whereas $PcFe(pyz)_2$ shows strong bands at 652 and 338 nm. On the other hand the visible spectrum of $[PcFe(pyz)]_n$ in benzene solution is not changed by excess pyz. Even if a very dilute solution of the polymer contains a 10^6 fold excess of pyz, the UV/VIS spectrum is unchanged after a two-month period at room temperature [23].

Spectroscopic results illustrate that the compound with the stoichiometric ratio PcFe : pyz = 1 : 1 cannot be a monomeric "PcFe(pyz)" having a pentacoordinated iron atom. This conclusion is consistent with kinetic measurements on related $PcFeL_2$ complexes [34–36], which show that a PcFe(II)L adduct (e.g. L = amine) is a reactive intermediate and immediately forms $PcFeL_2$ with excess ligand L.

Combined TG/DTA measurements show that $[PcFe(pyz)]_n$ is thermally more stable than $PcFe(pyz)_2$ (Table 1). The thermally induced dissociation range of the base (by TG) is 240–310 °C with a maximum of the DTA signal at 295 °C (endothermic). The observation, that pyz-bridged compounds are more stable than the corresponding monomeric compounds, was also made for a number of other pyz complexes [37].

IR Spectroscopy is a useful tool for distinguishing between the monomer $PcFe(pyz)_2$ and the bridged compound $[PcFe(pyz)]_n$. Pyrazine shows a characteristic centrosymmetric ring stretch [38–40] at about 1600 cm^{-1}, which is IR- and Raman-allowed for complexes containing unidentate pyz (as in $PcFe(pyz)_2$) and only Raman-allowed for bidentate (as in $[PcFe(pyz)]_n$) and for non-coordinated pyrazine [41]. This is caused by a higher local symmetry (D_{2h}) in the bidentate or free pyz compared with monodentate (terminal) pyz (C_{2v}). Therefore it is possible to classify pyrazine-containing complexes by means of this stretching absorption as compounds with pyrazine in a bridging or a terminal position. In the IR spectrum of $[PcFe(pyz)]_n$ there is a weak absorption present at 1582 cm^{-1}, but a strong intensity at this frequency is observed in monomeric $PcFe(pyz)_2$. Analysis of the intensities of this absorption has enabled us to determine the chain length *n* in $[PcFe(pyz)]_n$ as being greater than 20 [42].

^{57}Fe-Mössbauer measurements show comparable isomer shifts and quadrupole splittings for both $PcFe(pyz)_2$ and $[PcFe(pyz)]_n$ (Table 3), indicating a nearly identical environment for the iron atoms in both compounds [43].

Monomeric $PcML_2$ and bridged compounds $[PcM(pyz)]_n$ were also prepared with ruthenium (Ru^{2+}) and cobalt (Co^{2+}) as the central metal atom. $PcRuL_2$ complexes with L = pyz, 2-t-mepyz, 2,6-me$_2$pyz, bpy, 2-etpyz, 2t-bupyz, 2-Clpyz, pyridazine, and pyrimidine were prepared using the same methods as for the $PcFeL_2$ adducts [24,44]. Because of the good solubility of the $PcRuL_2$ adducts, NMR spectroscopy is a useful tool in elucidating the molecular structure of these compounds (Table 2). The ^{1}H NMR spectra of the above $PcRuL_2$ complexes show that they are diamagnetic (no paramagnetic line shift is detected) and have the expected $PcRuL_2$ stoichiometry. In case of the $PcRuL_2$ compounds with L = 2-mepyz, 2,6-me$_2$pyz, etpyz, t-bupyz and Clpyz, the NMR data show unambiguously that axial coordination to the central ruthenium atom takes place exclusively via the sterically non-hindered pyz nitrogen.

As expected, the shape of the UV/VIS spectra of the $PcRuL_2$ monomers is dominated by the intense *Q*-band around 640 nm and the *B*-band around 315 nm, which are due to transitions of the phthalocyaninato moiety. A weak absorption in the 450 nm range is characteristic of the nature of the axial ligand.

From the TG/DTA data of Table 1 it is evident that $PcRu(pyz)_2$ is clearly thermally more stable than the corresponding monomer $PcFe(pyz)_2$. Upon heating $PcRu(pyz)_2$, two endothermic DTA signals with maxima at 285 and 560 °C are observed, each corresponding to the separation of one pyz molecule from the monomer [24].

In contrast to $PcFe(pyz)_2$, monomeric $PcRu(pyz)_2$ does not split off one pyz in solution to form $[PcRu(pyz)]_n$. Therefore pure $[PcRu(pyz)]_n$ is not accessible by this route, but is obtained by heating $PcRu(pyz)_2$ to 300 °C. Under these conditions one pyz molecule is split off and $[PcRu(pyz)]_n$ is formed [24].

With the ligands L = py, pyz, mepyz, me$_2$pyz, bpy, and n-butylamine, PcCo prefers to form pentacoordinated complexes PcCoL. Hexacoordinated complexes $PcCoL_2$ are only formed at a high ligand concentration. $[PcCo(pyz)]_n$ was isolated as a stable compound [45]. To distinguish between penta- and hexa-coordinated cobalt complexes the usual spectroscopic methods were applied, including EPR spectroscopy and magnetic measurements [46a]. $PcRhL_2$ complexes (L = pyz, bpy) have also been synthesized recently [46b].

The influence of peripheral substituents at the phthalocyaninato moiety on the properties of the corresponding axial base adducts was studied with a number of substituted R_mPcM derivatives, which were synthesized for the first time ($m = 8$, $R = CH_3$, $M = Fe$; $R = OCH_3$, $M = Fe$, Co; $m = 16$, $R = Cl$, $M = Fe$; $m = 4$, $R =$ t-bu, $M = Fe$, Co; $R = NO_2$, $M = Co$) [47]. The coordination behaviour of the R_mPcFe derivatives was investigated with the unidentate ligand pyridine. The substituents R have a clear effect on the thermal stability of the $R_mPcFe(py)_2$ complexes. Electron donating substituents like CH_3 or OCH_3 decrease the thermal stability relative to $PcFe(py)_2$, while electron withdrawing Cl atoms are the cause of considerably higher thermal stability.

All the pyz-bridged compounds $[R_mFe(pyz)]_n$ (with octamethyl-, octamethoxy- or hexadecachloro-substituted phthalocyaninatoiron) are accessible in the same manner as $[PcFe(pyz)]_n$. Boiling of R_mPcFe with a slight excess of pyz in chlorobenzene for several days yields $[R_mPcFe(pyz)]_n$ [25]. With cobalt as the central metal, the substituted macrocycles R_mPcCo ($m = 4$, $R =$ t-bu, NO_2) can also be prepared. They coordinate with pyridine and substituted pyridines to form R_mPcCoL_2 adducts [48]. With pyz the dimeric complex $R_4PcCo(pyz)R_4PcCo$ ($R =$ t-bu) and the polymeric $[(NO_2)_4PcCo(pyz)]_n$ were isolated and characterized [48].

Other aromatic and non-aromatic metal macrocycles have been studied as their pyrazine adducts. These include tetraphenylporphine (TPPM), tetra(4-nitrophenyl)porphine (p-NO_2 TPPM), tetrabenzoporphyrine (TBPM), dihydrodibenzotetraaza[14]annulene (taaM), hemiporphyrazine (HpM), 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetra-decatetra-1,3,8,10-ene ($MTIM^{2+}$), tetramethyldihydrodibenzotetraaza[14]annulene (tmtaaM), 2,3-naphthalocyanine (2,3-NcM) and octaethylporphine (OEPM) which were used to prepare bridged compounds of the general type $[MacM(pyz)]_n$ (e.g. $M = Fe$). The experimental methods for the preparation of the pyz adducts are given in Scheme 1 [49–55].

It was possible to grow single crystals of the monomeric $TPPFe(pyz)_2$. The structure was solved by X-ray diffraction analysis [49,56]. Further the crystal structure [57] of the pyz-bridged bis-(dimethylglyoximato)(μ-pyrazine)cobalt(II) demonstrates that the pyrazine molecules within a chain are all arranged in a plane perpendicular to the plane of the planar bis(dimethylglyoximato)cobalt(II) moiety.

Other heterocycles containing more nitrogen atoms were also used for the preparation of monomeric and polymeric complexes with PcFe, PcRu and 2,3-NcFe as macrocycles [30,53,58]. Similar to the synthesis of $[PcFe(pyz)]_n$, $[PcFe(tz)]_n$ can be prepared using 1,2,4,5-tetrazine (tz) as the bridging ligand. $[PcRu(tz)]_n$ and $[2,3\text{-}NcFe(tz)]_n$ are prepared by a heterogeneous reaction of PcRu and 2,3-NcFe respectively with a slight excess of s-tetrazine at 70 °C

TPPFe p-NO_2TPPFe HpFe 2,3-NcFe $[FeTIM(CH_3CN)_2](PF_6)_2$	$\xrightarrow{\text{molten pyz}}$	TPPFe(pyz)$_2$ p-NO_2TPPFe(pyz)$_2$ HpFe(pyz)$_2$ 2,3-NcFe(pyz)$_2$ × 0.2 pyz $[FeTIM(pyz)_2](PF_6)_2$
$Ru(OEP)_2$ $Os(OEP)_2$ Fe(OEP)	$\xrightarrow{\text{excess pyz}}$	RuOEP(pyz)$_2$ OsOEP(pyz)$_2$ FeOEP(pyz)$_2$
PcFe	$\xrightarrow[\text{excess tz}]{CHCl_3/EtOH}$	PcFe(tz)$_2$
RcRu	$\xrightarrow[\text{excess tz}]{CHCl_3}$	PcRu(tz)$_2$
Fetaa Fetmtaa	$\xrightarrow{\text{molten pyz}}$	$[\text{Fetaa(pyz)}]_n$ $[\text{Fetmtaa(pyz)}]_n$
TPPFe p-NO_2TPPFe HpFe Fetaa Fetmtaa	$\xrightarrow[\text{slight excess of ligand}]{\text{heating in chlorobenzene}}$	$[\text{TPPFe(pyz)}]_n$ $[p\text{-}NO_2\text{TPPFe(pyz)}]_n$ $[\text{HpFe(pyz)}]_n$ $[\text{Fetaa(pyz)}]_n$ $[\text{Fetmtaa(pyz)}]_n$
$Ru(OEP)_2$ Os(OEP) Fe(OEP)	$\xrightarrow[\text{toluene}]{\text{slight excess of pyz}}$	$[\text{RuOEP(pyz)}]_n$ $[\text{OsOEP(pyz)}]_n$ $[\text{FeOEP(pyz)}]_n$
$[FeTIM(pyz)_2](PF_6)_2$	$\xrightarrow[CHCl_3/H_2O]{\text{extraction with}}$	$[FeTIM(\mu\text{-pyz})(H_2O)]_n$
2,3-NcFe(pyz)$_2$	$\xrightarrow{CHCl_3}$	$[\text{2,3-NcFe(pyz)} \times 0.2\ CHCl_3]_n$

Scheme 1.

in chlorobenzene. The preparation of a pure monomeric complex was only possible in the case of PcRu(tz)$_2$ by reacting PcRu with an excess of s-tetrazine. PcFe(tz)$_2$ could not be isolated in a pure state; due to its low solubility it could not be separated from non-reacted PcFe. 2,3-NcFe does not form a monomeric complex.

The ^{1}H NMR spectrum of the soluble PcRu(tz)$_2$ shows coordination of only one nitrogen atom of the tz molecule with the metal atom; an edge-on coordination of the ligands is excluded. The thermal stabilities of these compounds are lower in comparison with the corresponding pyz complexes, a result of the lower stability of tz. All the tz-coordinated iron compounds were further characterized by ^{57}Fe-Mössbauer spectroscopy. In comparison with the square-planar arrangement of the Fe atom in PcFe and 2,3-NcFe, the isomer shift δ and the quadrupole splitting ΔE_Q are in agreement with hexacoordination of the Fe^{2+} central metal atom in the monomers and bridged compounds listed in Table 3. Therefore pentacoordination can be excluded in the bridged $[PcFe(tz)]_n$ and $[2,3\text{-}NcFe(tz)]_n$ complexes. X-Ray powder diffraction data show that $[PcFe(tz)]_n$ and $[PcRu(tz)]_n$ are isomorphous.

1,4-Diazabicyclo[2.2.2]octane (dabco), a linear bidentate ligand with two nitrogen atoms, but without π-electrons, was used to synthesize a number of monomeric $MacM(dabco)_2$ and polymeric $[MacM(dabco)]_n$ compounds (MacM = PcFe, PcRu, PcCo, TPPFe) [23,45,49]. The $PcRu(dabco)_2$ adduct is soluble in $CHCl_3$, and ^1H NMR data are given in Table 2.

C. 4,4′-BIPYRIDINE AND RELATED COMPOUNDS AS AXIAL LIGANDS

While pyz, tz and dabco cause nearly the same inter-ring distance of ~ 680 pm (estimated) between two macrocycles in a polymer $[MacML]_n$, other ligands can be used to enlarge this inter-ring distance. These include

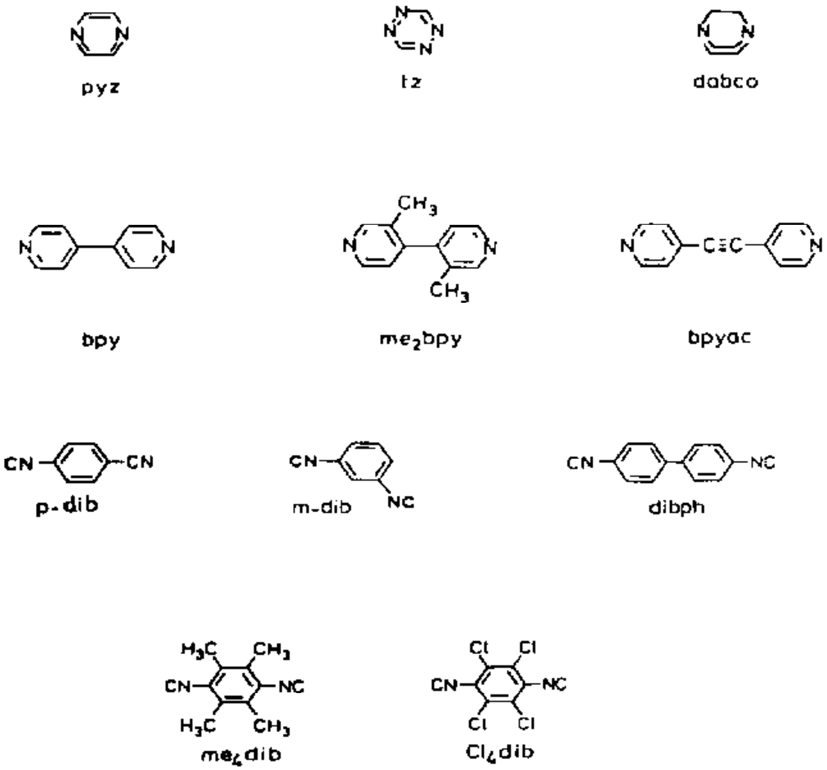


Fig. 3. Bridging ligands pyrazine (pyz), 1,2,4,5-tetrazine (tz), diazabicyclo[2.2.2]octane (dabco), 4,4′-bipyridine (bpy), 2,2′-dimethyl-4,4′-bipyridine (me_2bpy), bipyridylacetylene (bpyac), *p*-diisocyanobenzene (dib), *m*-diisocyanobenzene (*m*-dib), diisocyanobiphenyl (dibph), tetramethyldiisocyanobenzene (me_4dib) and tetrachlorodiisocyanobenzene (Cl_4dib).

ligands such as 4,4′-bipyridine (bpy) (with a distance of ~ 1110 pm between two macrocycles), 3,3′-dimethyl-4,4′-bipyridine (me_2bpy), 4,4′-bipyridylacetylene (bpyac) (distance 1320 pm) (see Fig. 3), *trans*-1,2-bis(4-pyridyl)ethylene (bpe), 1,2-bis(4-pyridyl)ethane (bpa) and 4,4′-trimethylene bipyridine (tmbpy).

A number of monomeric $MacML_2$ (L = bpy, MacM = PcFe, PcRu, TPPFe, 2,3-NcFe; L = me_2bpy, MacM = PcFe; L = bpyac, MacM = PcFe, PcRu, TPPFe, $Cl_{16}PcFe$), one dimeric complex ($[PcCo]_2(bpy)$) and various polymeric complexes $[MacML]_n$ (L = bpy, MacM = PcFe, PcRu, 2,3-NcFe, TPPFe; L = me_2bpy, MacM = PcFe; L = bpyac, MacM = PcFe, PcRu, TPPFe, Me_8PcFe, $Cl_{16}PcFe$; L = bpe, bpa, tmbpy, MacM = PcFe) have been reported [24,27,32,49,53,59,60].

The hexacoordinated compounds $MacML_2$ are prepared by reaction of MacM (Mac = Pc^{2-}, 2,3-Nc^{2-}, TPP^{2-}; M = e.g. Fe^{2+}, Ru^{2+}, Co^{2+}) in a melt of the ligand (bpy, me_2bpy and bpyac). The bridged compounds $[MacML]_n$ were synthesized either by refluxing MacFe (Mac = TPP^{2-}, Pc^{2-}) with a small excess of ligand in a suitable solvent or by splitting off one molecule of ligand from the monomer $MacML_2$ (L = bpy, MacM = 2,3-NcFe; L = bpyac, MacM = TPPFe, PcFe) in chloroform, chlorobenzene or toluene.

In the case of the bpy polymers IR spectroscopy is a useful method to distinguish monomeric from dimeric and polymeric compounds [42]. The monomeric derivatives $MacM(bpy)_2$ give rise to bands at 800, 1070, 1215, 1402 and 1589 cm^{-1}, caused by the ligand and they agree with the bands exhibited by free bpy. Compounds containing the bidentate bridged ligand differ in the IR spectra by the disappearance of the absorption at about 1215, 1402 and 1589 cm^{-1} [23,25,49]. For $[2,3\text{-NcFe(bpy)}]_n$ these absorptions appear but with reduced intensity, indicating that only a short oligomer is formed [53]. With bpyac as bridging ligand, definite assignment of the absorption sensitive to the coordination state is not possible. As usual thermal analysis confirms the metallomacrocycle to ligand ratio [60].

D. VARIOUS ISOCYANIDES AS AXIAL LIGANDS

1,4-Diisocyanobenzene (dib), and its derivatives tetramethyl- and tetrachlorodiisocyanobenzene (me_4dib, Cl_4dib), the 1,3-diisocyanobenzene (*m*-dib) and 4,4′-diisocyanobiphenyl (dibph) (see Fig. 3) [61] have been used as bridging ligands. Dib as a bridging ligand leads to a longer metal–metal distance than, for example, pyrazine, in the polymers $[MacML]_n$ (680 vs. 1190 ppm). The dib-bridged compounds, prepared in our laboratory are listed in Table 4. The macrocycles Pc [23], TPP [49], TBP [62], 2,3-Nc [63], 1,2-Nc [64] and TIM [52], were used with e.g. iron and ruthenium. For better

TABLE 4

IR and TG/DTA data of monomeric and polymeric macrocyclic metal complexes with bisaxial coordinated isocyanides

Compound	IR (ν_{NC}) (cm^{-1}) [a]		Dissociation range of base by TG [b] (°C)	Ref.
	Free ligand	Coordinated ligand		
[PcFe(dib)]$_n$	2130	2100	220 [c]	23
PcFe(dib)$_2$	2130	2105	–	65
[TPPFe(dib)]$_n$	2130	2083	290–375	49
[TBPFe(dib)]$_n$	2130	2080	230–280	62
TBPFe(dib)$_2$	2130	2098	–	62
[2,3-NcFe(dib)]$_n$	2130	2110	240 [c]	63
2,3-NcFe(dib)$_2$	2130	2124	235 [c]	63
[1,2-NcFe(dib)]$_n$	2130	2090	240–310	64
[TIMFe(dib)]$_n$(PF$_6$)$_{2n}$	2130	2135	–	52
[PcFe(me$_4$dib)]$_n$	2113	2092	255–350	66
PcFe(me$_4$dib)$_2$	2113	2109	–	66
[PcFe(Cl$_4$dib)]$_n$	2128	2058	260–350	66
[PcRu(dib)]$_n$	2130	2087	210 [c]	24
PcRu(dib)$_2$	2130	2095	–	24
[PcRu(me$_4$dib)]$_n$	2113	2084	255–350	66
PcRu(me$_4$dib)$_2$	2113	2092	–	66
[PcRu(Cl$_4$dib)]$_n$	2128	2038	255	66
[PcFe(dibph)]$_n$	2126	2113	275–500	66
PcFe(dibph)$_2$	2126	2130	–	66
[PcRu(dibph)]$_n$	2126	2101	250–450	66
PcRu(dibph)$_2$	2126	2122	–	66
[(CH$_3$)$_8$PcFe(dib)]$_n$	2130	2094	235 [c]	25
[(OCH$_3$)$_8$PcFe(dib)]$_n$	2130	2092	245 [c]	25
[Cl$_{16}$PcFe(dib)]$_n$	2130	2122	290 [c]	25
[(CH$_3$)$_8$PcFe(Cl$_4$dib)]$_n$	2128	2050	260 [c]	66
[PcFe(*m*-dib)]$_n$	2135, 2145	2098	230 [c]	60
PcFe(*m*-dib)$_2$	2135, 2145	2112 s, 2144 w	–	60
[PcRu(*m*-dib)]$_n$	2135, 2145	2083	–	24
PcRu(*m*-dib)$_2$	2135, 2145	2100 s, 2143 w	–	24
[(CH$_3$)$_8$PcFe(*m*-dib)]$_n$	2135, 2145	2082	225 [c]	60
[(OCH$_3$)$_8$PcFe(*m*-dib)]$_n$	2135, 2145	2078	195 [c]	60
[Cl$_{16}$PcFe(*m*-dib)]$_n$	2135, 2145	2114	260 [c]	60

[a] Nujol mull or KBr.

[b] Same conditions as in Table 1.

[c] Beginning of decomposition.

characterization of the dib-bridged compounds, the corresponding monomeric bisaxially coordinated complexes MacML$_2$ (L = dib, me$_4$dib, etc.) were also synthesized; however special methods had to be developed for the synthesis of these monomers. The synthesis cannot be carried out in the melt of the ligand as, for example, in the case of pyz monomers PcM(pyz)$_2$ (M = Fe, Ru), because dib and its derivatives do not have the same thermal stability as pyz. Treatment of MacM (Mac = Pc, TBP, 2,3-Nc; M = Fe, Ru) with a solution of dib in chloroform or acetone leads in the case of Mac = Pc, TBP, 2,3-Nc and M = Fe, Ru to MacM(dib)$_2$ [62,63,65]. Alternatively PcFe and PcRu react with aliphatic and aromatic monodentate isocyanides RNC (R = t-bu, c-hx, bz, ph, me$_2$ph) either in a solvent or in the melt with formation of the corresponding bisaxial substituted phthalocyaninatometal(II) compounds PcM(RNC)$_2$ (M = Fe, Ru) [66,67].

The bridged compounds [MacML]$_n$ (Mac = Pc, TBP, TPP, 2,3-Nc, 1,2-Nc, TIM; M = e.g. Fe, Ru; L = dib) were mostly synthesized by refluxing MacM with some excess of dib (about 1.1–3 mol) in chloroform, acetone or chlorobenzene for 48–72 h [23,49,62–65]. Another synthetic method is a ligand exchange reaction using MacM(py)$_2$ (Mac = e.g. TPP, M = e.g. Fe) as starting material, which is treated with a large excess of dib in chlorobenzene to form polymers [MacM(dib)]$_n$ (Mac = e.g. TPP; M = e.g. Fe) in good yields [49]. Both, polymers [MacML]$_n$ (Mac = Pc, TPP, TBP, 2,3-Nc, 1,2-Nc; M = e.g. Fe, Ru) and monomers MacML$_2$ (Mac = Pc, TBP, 2,3-Nc; M = e.g. Fe, Ru) are dark-colored powders and air stable. They were characterized by elemental analysis, thermal analysis (TG), differential thermal analysis (DTA), UV/VIS, IR and, if sufficiently soluble, by NMR spectroscopy.

The IR spectra of all isocyanide complexes [MacML]$_n$ and MacML$_2$ show the intense stretching frequency of the isocyanide group at about 2080–2150 cm^{-1} (see Table 4). The shift of this absorption on the change from free to metal-coordinated ligand is attributed to the σ-donor and π-acceptor character of the metal–ligand band. The strength of the π-acceptor bond depends on the central metal atom as well as on the electronic properties of the equatorial macrocycle. In [2,3-NcFe(dib)]$_n$ the NC-vibration is observed at higher frequency than in the analogous phthalocyanine and porphyrine derivatives (see Table 4). In general all the polymeric isocyanide compounds listed in Table 4 exhibit much stronger π-back-bonding than the monomeric species MacML$_2$. This can be observed in the IR spectra because an increase of the π-back-donation leads to a decrease of the NC-valence frequency since π-back-bonding occurs to a strongly antibonding orbital.

The IR NC-frequency is also influenced by peripheral substitution of the macrocycle in the polymers [R$_8$PcFeL]$_n$ (R = CH$_3$, OCH$_3$; L = dib, m-dib) and [Cl$_{16}$PcFeL]$_n$ (L = dib, m-dib) [25,60]. Electron donating substituents, such as methyl and methoxy, shift the vibration-frequency of the NC-bond to lower energy, while electron withdrawing substituents such as chlorine induce a shift to higher energy. Examples are listed in Table 4.

TABLE 5

IR and TG/DTA data of monomeric unidentate isocyanide macrocyclic metal complexes

Compound	IR (ν_{NC}) (cm^{-1}) [a]		Dissociation range of base by TG (°C)	Ref.
	Free ligand	Coordinated ligand		
PcFe(t-buNC)$_2$	2138	2150	165–250	67
TBPFe(t-buNC)$_2$	2138	2132	–	54
2,3-NcFe(t-buNC)$_2$	2138	2147	165 [c]	69
1,2-NcFe(t-buNC)$_2$	2138	2140	140–230	64
PcRu(t-buNC)$_2$	2138	2143	165–250	67
TPPRu(t-buNC)$_2$	2138	2106 [d]	–	68
PcFe(c-hxNC)$_2$	2138	2157	200–290	67
TBPFe(c-hxNC)$_2$	2138	2137	–	54
2,3-NcFe(c-hxNC)$_2$	2138	2164	210–300	69
1,2-NcFe(c-hxNC)$_2$	2138	2155	170–260	64
PcRu(c-hxNC)$_2$	2138	2153	240–350	67
PcFe(phNC)$_2$	2126	2120	180–265	67
TBPFe(phNC)$_2$	2126	2105	–	54
PcRu(phNC)$_2$	2126	2110	230–310	67
PcFe(bzNC)$_2$	2151	2165	200–290	67
2,3-NcFe(bzNC)$_2$	2151	2166	130–280	69
1,2-NcFe(bzNC)$_2$	2151	2153	175–270	64
PcFe(me$_2$phNC)$_2$	2122	2122	225–295	67
PcRu(me$_2$phNC)$_2$	2122	2119	295–410	67
PcRu(me$_2$phNC)	2122	2074	350–410	66
PcFe(Cl$_4$phNC)$_2$	2133, 2125	2089	235–340	66
PcRu(Cl$_4$phNC)$_2$	2133, 2125	2075	280–435	66
PcRu(Cl$_4$phNC)$_2$	2133, 2125	2025	370–435	66

[a] Nujol mull or KBr.

[b] Same conditions as in Table 1.

[c] Beginning of decomposition.

[d] In benzene.

In the monomeric isocyanides MacML$_2$ (Mac = Pc, TBP, 2,3-Nc, 1,2-Nc; M = e.g., Fe, Ru; L = e.g., dib, me$_4$dib, dibph, *m*-dib, t-buNC, c-hxNC, bzNC, phNC, me$_2$phNC, Cl$_4$phNC) the NC absorption is sometimes shifted to higher frequency than observed in the free ligand. It is always shifted to higher frequency in comparison with the absorption of the polymer, indicating that mostly σ-donation is involved (Tables 4 and 5) [23–25,27,49,52,54, 60,62–69].

NMR spectroscopy can only be used for identification of soluble monomeric isocyanides MacML$_2$ (Mac = Pc, TBP, 2,3-Nc, 1,2-Nc; M = e.g., Fe, Ru; L = dib, bzNC, phNC, me$_4$dib, me$_2$phNC, Cl$_4$phNC, *m*-dib) [25,54,60,62,64,66,67,69] (for some examples see Table 6). ^{1}H NMR spectroscopy proves to be a common and definitive method for the structure

TABLE 6

^{1}H NMR Data of some macrocyclic metal isocyanide adducts [a]

Compound	Coordinated ligand	Free ligand	Macrocycle	Ref.
PcFe(bzNC)$_2$	2.49 *s*, 5.00 *d* 6.46 *t*, 6.73 *d*	4.57, 7.30	7.98, 9.31	23
TBPFe(dib)$_2$	4.84, 6.30	7.41 *s*	8.03, 9.38 10.61 [b]	62
PcFe(phNC)$_2$	5.15, 6.39 6.59	7.38	8.00, 9.35	67
TBPFe(phNC)$_2$	4.83, 6.35	7.38	7.95, 9.37 10.60 [b]	54
PcFe(me$_4$dib)$_2$	0.07 *s*, 1.59 *s*	2.37 *s*	8.00, 9.34	66
PcFe(me$_2$phNC)$_2$	6.07 *d*, 6.35 *t* 0.18 *s*	7.1, 2.40 *s*	7.97, 9.33	67
PcFe(Cl$_4$phNC)$_2$	6.64 *s*	7.65 *s*	7.99, 9.30	66
PcFe(*m*-dib)$_2$	6.64, 6.49 5.18	7.42 *m*	8.03, 9.36	60

[a] Chemical shifts in ppm; $CHCl_3$ as internal standard.

[b] Proton of the methine group connecting the 4 isoindole units in tetrabenzoporphyrine.

determination of soluble axially coordinated phthalocyaninatoiron- and ruthenium(II)-complexes. The ratio PcM : RNC = 1 : 2, which follows from the integration, shows the hexacoordination of the central metal atom according to PcM(RNC)$_2$. In the case of the phthalocyaninatometal compounds the Pc-protons appear as a typical AA′BB′ system at a low field centered round 9 and 8 ppm respective due to the strong ring current of the heteroaromatic 18 π-electron system. The protons of the axial ligands are in general shifted to a higher field [67]. For further characterization of the PcM(RNC)$_2$ monomers, (M = Fe, Ru) with the above mentioned substituents ^{13}C NMR spectroscopy was also applied [67]. The isocyanide-C-atom signal is shifted upfield ~ 10 ppm for PcFe(RNC)$_2$ complexes and ~ 20 ppm for the corresponding PcRu(RNC)$_2$ complexes respectively upon coordination to the central metal atom.

The NMR spectra can often only be measured in $CDCl_3$ solution, containing an excess of the ligand to avoid dissociation or polymerization.

The influence of substituents at the axially coordinated ligands on the physical properties was studied systematically with the monomers PcM(Me$_4$dib)$_2$ (M = Fe, Ru) and the polymers [PcM(me$_4$dib)]$_n$, [PcM(Cl$_4$dib)]$_n$ and [PcM(dibph)]$_n$ (M = Fe, Ru), with 2,3,5,6-tetramethyl-1,4-diisocyanobenzene (me$_4$dib), 2,3,5,6-tetrachloro-1,4-diisocyanobenzene (Cl$_4$dib) and 4,4′-diisocyanobiphenyl (dibph) as the axial ligands [66].

The bidentate ligand me$_4$dib reacts with PcFe and PcRu yielding bisaxially coordinated monomeric complexes PcM(me$_4$dib)$_2$ (M = Fe, Ru) or the one-dimensional bridged polymeric chain structures $[PcM(me_4dib)]_n$ (M = Fe, Ru) depending on the reaction conditions. Cl_4dib also forms the corresponding polymers $[PcM(Cl_4dib)]_n$ (M = Fe, Ru). The synthesis of the bridged complexes is also possible starting with the monomers $PcM(me_4dib)_2$ (M = Fe, Ru) in solution or in the solid state.

For the first time it was possible to follow the formation of $[PcM(me_4dib)]_n$ (M = Fe, Ru) by ^1H NMR spectroscopy in solution and thereby gain some information about the mechanism of formation of the bridged complexes. The monomers $PcM(me_4dib)_2$ (M = Fe, Ru), which are soluble in $CDCl_3$, were characterized by ^1H NMR spectroscopy [66].

If the NMR spectra of $PcM(me_4dib)_2$ (M = Fe, Ru) are not recorded directly after preparation of the solutions, additional weaker groups of signals having their centers at 9.30 and 7.97 ppm are observed. They appear at higher field compared to the signals of the Pc protons of the monomers, with centers at 9.34 and 8.00 ppm. These new signals are the result of dissociation of the monomers $PcM(me_4dib)_2$ to form dimers $(me_4dib)PcM(me_4dib)PcM(me_4dib)$ and trimers $(me_4dib)[PcM(me_4dib)]_2\,PcM(me_4dib)$ [66] (see Fig. 4). The methyl substitution of the dib ligand renders the definite characterization of these oligomers possible. In the dimer the signals of the terminal me_4dib ligands are shifted to higher field, while the protons of the bridged inner ligand are chemically equivalent and the signal is a singlet (see Table 7). The multiplets of the Pc ring system of the trimer are shifted even further upfield than those of the monomer and dimer (see Table 8). The phthalocyanine protons in the 3,6-position are shifted more than those in 4,5-position. The reason is that the ring currents of cofacially arranged phthalocyanine rings influence each other. This interaction however is reduced by the bridging ligand me_4dib [66].

In contrast to the diisocyanobenzene compounds $[PcM(dib)]_n$ and $PcM(dib)_2$ (M = Fe, Ru) the me_4dib and Cl_4dib products give information on the molar ratio of metallomacrocycle to ligand in TG/DTA. Me_4dib is volatile without decomposition, Cl_4dib decomposes slightly, but its rest mass loss can be accounted for by elemental analysis (Cl-value) of the TG-residue. In general me_4dib- and Cl_4-dib-polymers, $[PcM(me_4dib)]_n$ and $[PcM(Cl_4dib)]_n$ (M = Fe, Ru), exhibit higher thermal stabilities in comparison with the dib compounds [66].

Like peripheral substitution of the macrocycles, substitution of the bridging ligand also influences the position of the NC frequency in the IR spectra. As expected, me_4dib and dibph act only as weak π-acceptor ligands, while Cl_4dib is much stronger (see Table 4).

A non-linear bidentate unsymmetrically substituted ligand 1,3-diisocyanobenzene (*m*-dib) has been used for the preparation of phthalocyaninatometal complexes. The polymers and monomers with *m*-dib,

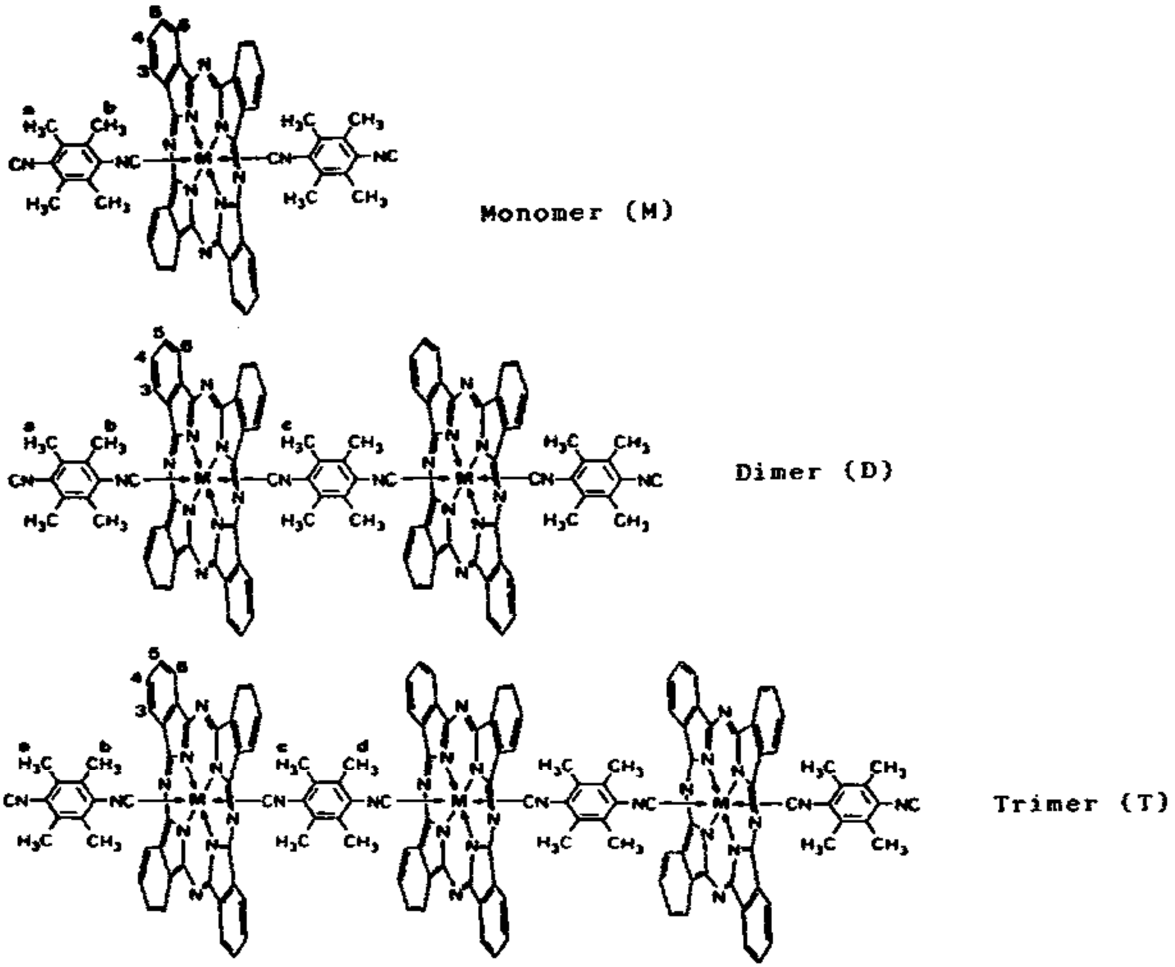


Fig. 4. Schematic drawing of the me$_4$dib-coordinated monomer, dimer and trimer.

TABLE 7

^{1}H NMR data of me$_4$dib-PcRu and PcFe complexes [a]

Compound	H [a]	H [b]	H [c]	H [d]
PcFe(me$_4$dib)$_2$	1.59	0.07	–	–
Dimer	1.51	−0.07	−0.71	–
PcRu(me$_4$dib)$_2$	1.60	0.08	–	–
Dimer	[b]	−0.06	−0.69	–
Trimer	[b]	−0.05	−0.76	−0.82

[a] In ppm; $CDCl_3$ as internal standard [66].

[b] Peak covered by H_2O.

TABLE 8

Incremental isoshielding of the ring protons for the oligomers of $PcRu(me_4dib)_2$ in ppm [66]

	3,6-Protons			4,5-Protons		
	Outer ring exper.	Incremental shift	Inner ring calc.	Outer ring exper.	Incremental shift	Inner ring calc.
Monomer	9.30		–	7.97		–
Dimer	9.10	−0.20	–	7.86	−0.10	–
Trimer	8.89	−0.20	8.90	7.73	−0.13	7.77

$[R_mPcM(m\text{-dib})]_n$ ($m = 8$; R = H, Cl; M = e.g. Fe, Ru) and $PcM(m\text{-dib})_2$ (M = Fe, Ru) as ligand can be synthesized using the same methods as in the case of the dib or me_4dib compounds $[PcM(dib)]_n$ and $[PcM(me_4dib)]_n$. The characterization however is more difficult [24,60]. The IR spectrum of the free m-dib ligand shows 3 NC frequencies. $PcM(m\text{-dib})_2$ and $[R_mPcM(m\text{-dib})]_n$ (M = Fe, Ru) show the same behaviour with respect to the shift of the CN frequencies compared to $PcM(dib)_2$ (M = Fe, Ru) and $[PcM(dib)]_n$.

The ^{57}Fe-Mössbauer data for monomeric and polymeric complexes with isocyanides as ligand are listed in Table 9. The quadrupole splitting ΔE_Q in these complexes is notably smaller than in other compounds $PcFeL_2$ with L = N-donor ligands, the isomer shift δ is also reduced. The value of ΔE_Q for $[me_8PcFe(Cl_4dib)]_n$ is the smallest reported for $PcFeL_2$ complexes till now. Similar behaviour was observed in $PcFe(CO)_2$ [18], and another example is the low spin Fe^{3+} complex $(PNP)[PcFe(CN)_2]$ (PNP^+ = bis(triphenylphosphine)nitrogen(1 +)) [19]. The reasons for that behaviour are not fully understood; for a discussion see refs. 18, 19.

TABLE 9

^{57}Fe Mössbauer data for iron(II)phthalocyanines with isocyanides as axial ligands [27] ($T = 293$ K)

Complex	δ (mm s^{-1}) [a,b]	ΔE_Q (mm s^{-1}) [b]
$PcFe(t\text{-}buNC)_2$	0.16(3)	0.79(5)
$PcFe(c\text{-}hxNC)_2$	0.13(1)	0.69(3)
$PcFe(phNC)_2$	0.11(0)	0.67(8)
$PcFe(me_2phNC)_2$	0.12(2)	0.70(2)
$PcFe(Cl_4phNC)_2$	0.09(5)	0.67(5)
$PcFe(me_4dib)_2$	0.11(7)	0.65(8)
$[PcFe(me_4dib)]_n$	0.14(2)	0.69(7)
$[PcFe(Cl_4dib)]_n$	0.06(6)	0.74(5)
$[me_8PcFe(Cl_4dib)]_n$	0.07(0)	0.58(2)

[a] Relative to metallic iron.

[b] Fit to a quadrupole doublet.

E. ELECTRICAL CONDUCTIVITY OF THE BRIDGED COMPLEXES

Polymerization of MacM (Mac = Pc, TBP, 2,3-Nc, OEP; M = e.g. Fe, Ru, Co) using bidentate ligands such as pyz, bpy, tz, etc. results in a clear increase of the conductivities by a factor of 10^3–10^7 in comparison with the corresponding monomers $MacML_2$. Temperature dependent electrical conductivities, measured as compressed pellets, show the semiconducting properties of the materials with typical activation energies between 0.1–0.4 eV. In Table 10 are listed the electrical conductivities of some selected polymer examples. The electrical properties of these compounds are described in more detail in refs. 1 and 55.

Many of the compounds $[MacML]_n$ are dopable either chemically, e.g. with iodine, nitrosyl hexafluorophosphate or other oxidants, or electrochemically [70,71]. Doped polymers show a drastic increase in conductivity relative to the undoped compounds. For example doping of $[PcFe(pyz)]_n$ or $[Ru(OEP)pyz]_n$ with iodine yields stable compounds with the stoichiometry $[PcFe(pyz)I_y]_n$ ($I_y = 0$–2.6) [43] and $[Ru(OEP)pyzI_y]_n$ ($y = 0.6$) respectively [55].

As in the case of the pyz compounds the dib-bridged macrocyclic compounds exhibit good semiconducting behaviour. In general the conductivi-

TABLE 10

Electrical conductivity of some bridged macrocyclic metal compounds

Complex	σ (S cm^{-1})	Ref.
$[PcFe(pyz)]_n$	2×10^{-5} [a]	23
$[PcRu(pyz)]_n$	1×10^{-7} [a,b]	24
$[TPPFe(pyz)]_n$	2×10^{-8} [c]	49
$[Fe(OEP)pyz]_n$	1×10^{-10} [b]	55
$[Ru(OEP)pyz]_n$	1×10^{-8} [a,b]	55
$[PcFe(tz)]_n$	0.02 [a]	30
$[PcRu(tz)]_n$	0.01 [a]	30
$[2,3\text{-}NcFe(tz)]_n$	0.3 [a]	30
$[PcFe(bpy)]_n$	2×10^{-8} [b]	23
$[PcFe(bpe)]_n$	2×10^{-7} [c]	32
$[PcFe(bpyac)]_n$	1×10^{-7} [a]	60
$[PcFe(dib)]_n$	2×10^{-5} [a]	23
$[PcRu(dib)]_n$	2×10^{-6} [a]	24
$[TBPFe(dib)]_n$	2×10^{-6} [a]	62
$[2,3\text{-}NcFe(dib)]_n$	2×10^{-3} [a]	63
$[PcFe(me_4dib)]_n$	1×10^{-7} [a]	66

[a] Four-probe-method.

[b] Two-probe-method.

[c] Unknown.

ties of the dib-bridged macrocyclic compounds increase in comparison with the corresponding monomers by several orders of magnitude. The polymers can also be doped with iodine leading to a considerable increase in conductivity. Some examples of the electrical conductivity are given in Table 10; for further details see ref. 1a.

F. SUMMARY

As described in this review, a variety of transition metal macrocyclic complexes can be easily reacted with N- and C-donor ligands L to form bisaxially coordinated monomers $MacML_2$. Also, "shish kebab"-bridged polymers MacMLMacML... can be synthesized with suitable bidentate bridging ligands. Most of the compounds are thermally quite stable and exhibit interesting spectroscopic and electrical properties.

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