Structural Investigations of Tetra- and Octasubstituted (Phthalocyanine)ruthenium Complexes by EXAFS Spectroscopy

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To obtain more structural information of (phthalocyaninato)-ruthenium compounds, an EXAFS investigation was carried out on amorphous tBu$_4$PcRu (**1**), tBu$_4$PcRu(3-Clpy)$_2$ (**2**), PcRu(3-Fpy)$_2$ (**3**) and (C$_5$H$_{11}$O)$_8$PcRu(3-Clpy)$_2$ (**4**). Structural models for the four compounds are deduced from the atomic distances determined around the metal centre. A dimeric structure was found for **1**, while bisaxial arrangement of the ligands was shown for **2, 3** and **4**, and the structural parameters were also determined.

Introduction

In recent years (phthalocyanine)ruthenium complexes have been investigated with particular regard to their preparation, chemistry, and structure.[1−3] Some years ago, we reported the first synthesis of pure (phthalocyananinato)ruthenium(II) (PcRu) by thermal decomposition of PcRu(DMSO)$_2$·2DMSO.[4] Later, we developed a convenient method for obtaining PcRu from the corresponding bis-(isoquinoline) complex PcRu(iqnl)$_2$, which decomposes at 250 °C with formation of pure PcRu.[5]

Due to the insolubility of PcRu − like most other (phthalocyanine)metal complexes − in common organic solvents, bulky (e.g. *tert*-butyl) or long-chain (e.g. alkyl or alkyloxy) groups are introduced onto the periphery of the Pc macrocycles to improve their solubility. The *tert*-butyl group is particularly suitable for increasing the solubility of phthalocyanines in organic solvents. Tetrasubstituted phthalocyanines usually exhibit higher solubilities than the octasubstituted analogues. The two principal reasons are that the isomeric mixture of four tetrasubstituted phthalocyanines leads to a lower degree of order in the solid state compared to the symmetrically octasubstituted phthalocyanines, and the higher dipole moment of the tetrasubstituted Pcs caused by the unsymmetrical arrangement of the substituents on the periphery of the macrocycle.[2] [Tetrakis(*tert*-butyl)phthalocyaninato]ruthenium(II) tBu$_4$PcRu (**1**),[6a] bis(3-chloropyridine)[tetrakis(*tert*-butyl)-phthalocyaninato]ruthenium(II) tBu$_4$PcRu(3-Clpy)$_2$ (**2**)[6a] (all mixtures of structural isomers), and several (octaalkyloxyphthalocyaninato)ruthenium compounds[5,6b,6c] are examples of soluble (phthalocyanine)ruthenium complexes. The thermal decomposition of the peripherally substituted R$_m$PcRu(3-Clpy)$_2$ provided the basis for the preparation of novel bridged [R$_m$PcRu(L)]$_n$ oligomers with L = pyz (pyrazine), dib (1,4-diisocyanobenzene), tz (*s*-tetrazine), and others as a new class of intrinsic semiconductors.[2,6b]

The crucial problem in the exact structural determination of (phthalocyanine)ruthenium compounds (PcRu) is that most of the compounds can only be prepared as amorphous or microcrystalline samples. In a previous paper we reported EXAFS studies on dimeric PcRu.[7] Our results are consistent with a dimeric structure having a short Ru−Ru contact of 2.41 Å. This agrees with LAXS investigations on the same system.[3] The existence of a Ru−Ru double bond is also confirmed by measurement of the magnetic moment, which amounts to 2.54 μ_B at room temperature.[7]

Now the question arises as to whether the formation of dimers is restricted to PcRu or whether it is a common phenomenon of (phthalocyanine)ruthenium compounds. There are some indications for the latter assumption, for example the magnetic moment of tBu$_4$PcRu has a value which is similar to PcRu.[6a] Temperature-dependent measurements of the magnetic susceptibility show **1** to exhibit paramagnetic behaviour with strong coupling. The magnetic moment increases from 0.63 μ_B (T = 20 K) to 1.68 μ_B (T = 300 K), i.e. it approximates asymptotically the spin-only value of one unpaired electron (1.73 μ_B). Compound **1** therefore has only one spin per ruthenium(II) ion, although for a d^6 transition metal ion in a square-planar ligand field two unpaired electrons are expected. This implies that **1** exists as a dimeric structure with a ruthenium−ruthenium double bond. For homometallic (porphyrin)metal dimers a molecular orbital diagram was developed[8] which proposes that only d electrons participate in metal−metal bonding. In addition, the reasonable assumption that the dimers have D_{4h} (eclipsed) or D_{4d} (staggered) symmetry was made. The σ bonds to the porphyrin nitrogen atoms involve the metal $d_{x^2-y^2}$ levels, and the high-energy σ* orbitals may be ig-

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nored for a metal-metal bonding.[8] The remaining d orbitals (d_{xz}, d_{yz}, d_{z^2}, and d_{xy}) are available for the metal−metal bonding along the *z* axis. Dimeric (porphyrin)- as well as (phthalocyanine)ruthenium(II) complexes possess 12 d-electrons and consequently the resulting electronic configuration, $\sigma^2\pi^4\delta^{nb4}\pi^{*2}$, produces a formal Ru−Ru double bond with two unpaired electrons (one per macrocycle). On the other hand one has to take into consideration that the four *tert*-butyl groups in **1** could cause steric hindrance if a dimeric structure is formed as in PcRu.

In order to answer these questions we performed EXAFS measurements on *t*Bu$_4$PcRu (**1**). In addition we carried out EXAFS measurements on *t*Bu$_4$PcRu(3-Clpy)$_2$ (**2**), PcRu(3-Fpy)$_2$ (**3**) and $(C_5H_{11}O)_8$PcRu(3-Clpy)$_2$ (**4**), for which crystal structures are not yet available, to obtain some structural data of these bissubstituted PcRu complexes. Furthermore, we intended to prove whether the different ligands are arranged in a strictly bisaxial disposition, and whether the different ligands (3-chloropyridine in **2** and **4**, 3-fluoropyridine in **3**) or the different phthalocyanine macrocycles [unsubstituted (**3**), 2,3-tetra- (**2**) and 1,4-octa-substituted (**4**) (see Figure 4)] have any structural effects on the local environment around the ruthenium centre.

Results and Discussion

[Tetrakis(*tert*-butyl)phthalocyaninato]ruthenium(II) (1)

As can be seen in the Fourier transform (see Figure 1b), there are several visible shells. In fitting the EXAFS function, we must describe it by at least six shells. Fitting the data by six shells seems to be many, but is not for two reasons. First, the coordination numbers were fixed to the known values of the phthalocyanine molecule. Second, the four shells of the phthalocyanine macrocycle marked with A in Table 1 (see Figure 2) can only be independently fitted such that the determined distances lead to meaningful interatomic distances in the macrocycle itself. Taking these considerations into account, the number of parameters decreases from 12 to 9 and are clearly less than the number of independent data points (22).[9] We successfully applied this data evaluation in previous work on (phthalocyaninato)ruthenium.[7]

Without any knowledge of the structure, one would expect that the ruthenium atom is located in the plane of the phthalocyanine ring. A planar arrangement of the atoms should give rise to a considerable contribution of multiple scattering to the EXAFS spectrum. Defining the multiple scattering unit as shown in Figure 3, we found in several calculations that for this geometrical arrangement the relevant maximum order of multiple scattering is three. But in all fits we could not describe the experimental spectrum satisfactorily. In particular, the characteristic features of the experimental $k^3\cdot\chi(k)$ function between 4.0 and 9.0 Å^{-1} could not be reproduced (see Figure 1c).

Since only single scattering contributes to the EXAFS function, we are forced to assume that either the ruthenium atom is not positioned in the plane of the ring, or the ring

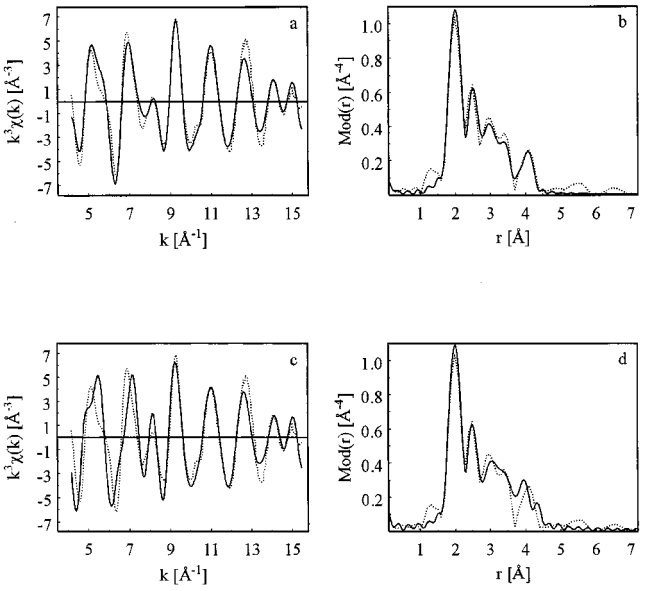

Figure 1. Experimental (dotted line) and calculated (solid line) $k^3\cdot\chi(k)$ function (a,c) (k range: 3.50−15.30 Å^{-1}) and their Fourier transforms (b,d) of *t*Bu$_4$PcRu (**1**) [see Table 1 for fitting parameters, considering single scattering only (a,b), including triple scattering paths (c,d)]

Table 1. EXAFS-determined structural data of **1**

[a]		*R* [Å]	*N*	σ [Å]	ΔE_0 [eV]	Fit index
Ru−N	(A)	2.01±0.02	4.0	0.055±0.009	19.96	25.91
Ru−C	(A)	3.05±0.03	8.0	0.067±0.011		
Ru−N	(A)	3.23±0.03	4.0	0.039±0.009		
Ru−C	(A)	4.04±0.04	8.0	0.071±0.009		
Ru−Ru	(B)	2.42±0.03	1.0	0.077±0.011		
Ru−N	(B)	3.38±0.03	4.0	0.040±0.009		

[a] Absorber−backscatterer distance *r*, coordination number *N* and Debye-Waller factor σ with their calculated standard deviation. The letters in parentheses refer to the model in Figure 2 and indicate the molecule where the backscattering atom is located.

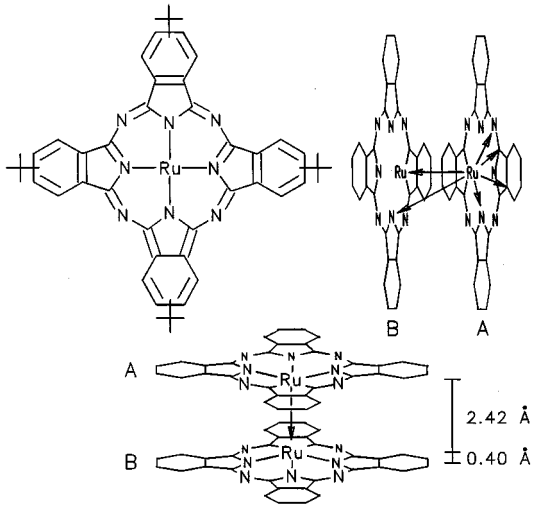

Figure 2. Structural model of *t*Bu$_4$PcRu (**1**) including the assignment of the determined distances to the corresponding atoms (see Table 1); for reasons of clarity, not all nitrogen atoms and *tert*-butyl groups are shown

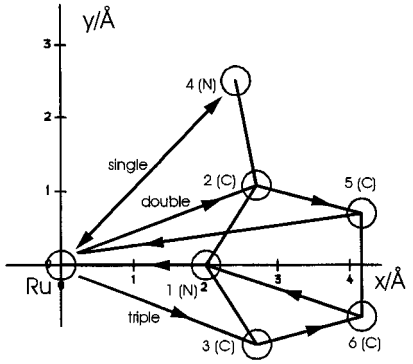

Figure 3. Defined multiple scattering unit for tBu$_4$PcRu (**1**) illustrating single, double and triple scattering paths

itself is not planar, or both. In order to check the dependence of the amount of multiple scattering from the out-of-plane displacement of the ruthenium atom in an idealized planar macrocycle we performed systematic calculations. We found the rather astonishing result that the amount of multiple scattering does not depend very strongly on the out-of-plane position of the ruthenium atom. Only if the displacement amounts to 1.75 Å does the contribution of the multiple scattering almost vanish. Since such a large displacement of the ruthenium atom is quite unlikely, we have to conclude that the nonplanarity of the macrocycle is the main cause of the absence of any multiple scattering and the possible displacement of the ruthenium atom − if existing − plays only a minor role. From the determined distances it is not possible to make any structural statements concerning the nonplanarity of the macrocycle.

Besides the four shells of the phthalocyanine macrocycle already discussed, a significant improvement in the fit index can be obtained if we assume a Ru−Ru distance of 2.42 Å in the simulation of the spectrum. Additionally, we found four nitrogen backscatterers at 3.38 Å. These distances can be assigned to the corresponding atoms in the macrocycle B (see Figure 2 and Table 1). In the context of the above discussion regarding the absence of any multiple scattering and the possible explanation for this, the presence of a Ru−Ru interaction at a distance of 2.42 Å is surely an indication that besides the nonplanarity of the macrocycle, an out-of-plane displacement of the ruthenium atom is also to a small degree responsible for the absence of any multiple scattering. Without the displacement, it is probably impossible to get the two ruthenium atoms this close. If we make the simplified assumption that the four nitrogen atoms of the phthalocyanine macrocycle forming the first coordination shell lie in a plane, the displacement of the ruthenium atom can be appraised in the following way. From crystallographic data[10,11] we know that the metal−nitrogen distance of planar systems, e.g. in phthalocyaninatomanganese tetracyanoethenide, is typically 1.97±0.3 Å. As an N−N diagonal distance of 3.94±0.6 Å follows from this value, we can calculate that the ruthenium atom is located 0.4±0.2 Å out of the plane of the macrocycle (see Figure 2). We note that this triangulation depends critically on both the measured Ru−N distance and the assumed N−center distance. It is given here only as a rough estimation of the amount of the possible displacement. Our data are also compatible with an in-plane geometry for **1**.

[Bis(3-chloropyridine)[tetrakis(*tert*-butyl)phthalocyaninato]-ruthenium(II) (2)

For a similar quality simulation of the EXAFS function of compound **2** (see Figure 4), at least six shells are necessary (see Table 2 and Figure 5a and 5b). These are the four shells of the phthalocyanine macrocycle and two nitrogen backscatterers at 2.53 Å, which can only be assigned to the ligand 3-chloropyridine, because no ring atoms are located within this distance. Furthermore, there are four carbon backscatterers at a distance of 3.43 Å, which also belong to 3-chloropyridine. As can be seen in Figure 5c and 5d, the four carbon backscatterers at 3.43 Å are necessary for a complete description of the experimental EXAFS function.

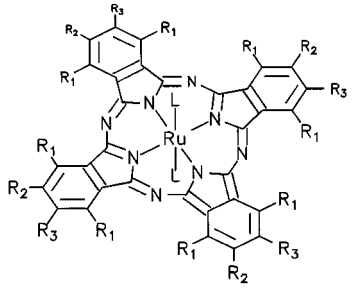

Figure 4. Schematic structural model of R$_n$PcRu(L)$_2$ (**2** for R$_2$ or R$_3$ = tBu, R$_1$ = H and L = 3-chloropyridine, **3** for R$_1$ = R$_2$ = R$_3$ = H and L = 3-fluoropyridine, **4** for R$_2$ = R$_3$ = H, R$_1$ = R$_4$ = C$_5$H$_{11}$O and L = 3-chloropyridine)

Table 2. EXAFS-determined structural data of **2**

[a]		R [Å]	N	σ [Å]	ΔE_0 [eV]	Fit index
Ru−N	(A)	2.03±0.02	4.0	0.060±0.009	19.13	21.74
Ru−C	(A)	3.07±0.03	8.0	0.056±0.009		
Ru−N	(A)	3.31±0.03	4.0	0.053±0.009		
Ru−C	(A)	4.00±0.04	8.0	0.075±0.010		
Ru−N	(L)	2.53±0.03	2.0	0.086±0.011		
Ru−C	(L)	3.43±0.03	4.0	0.048±0.009		

[a] Absorber−backscatterer distance r, coordination number N and Debye-Waller factor σ with their calculated standard deviation. The letters in parentheses refer to the model in Figure 4 and indicate the molecule where the backscattering atom is located.

With the distances to the ligand determined as Ru−N (2.53 Å) and Ru−C (3.43 Å), an N−C distance in 3-chloropyridine of 1.38 Å can be calculated (see Figure 6), in good agreement with the expected value of 1.34 Å for the intramolecular C−N distance in pyridine.[12] In one of our previous works[7] we found an Ru−Ru distance at 4.14 Å in PcRu(nBuNH$_2$)$_2$. No Ru−Ru distance in this range could be found in **2**. These results led us to the conclusion that the 3-chloropyridine molecule is vertically located below and above the phthalocyanine macrocycle and forms an octahedral arrangement around the ruthenium centre (see Figure 4 and Figure 6) together with the four nitrogen

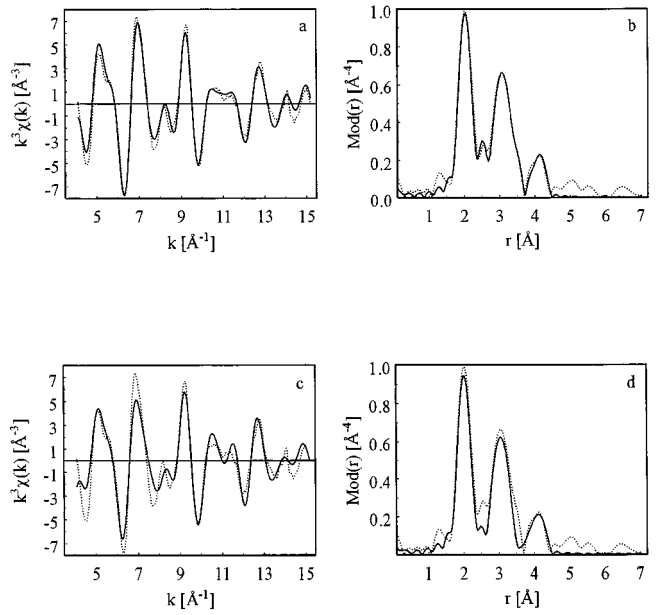

Figure 5. Experimental (dotted line) and calculated (solid line) $k^3 \cdot \chi(k)$ function (a,c) (k range: 3.45−15.15 Å^{-1}) and their Fourier transforms (b,d) of tBu$_4$PcRu(3-Clpy)$_2$ (**2**) [see Table 2 for fitting parameters, six shells model (a,b) and five shells model (c,d), respectively]

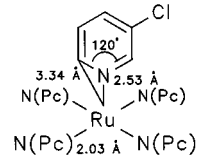

Figure 6. A detailed view from Figure 4; the ligand, the ruthenium centre and the first nitrogen backscatterers are shown

atoms of the phthalocyanine macrocycle. The axial coordination of the 3-chloropyridine ligand prevents the formation of a dimeric phthalocyanine unit coupled over an Ru−Ru double bond. The absence of any multiple scattering in **2** is surely only a result of the nonplanarity of the macrocycle and an out-of-plane displacement is very unlikely. This is because this displacement would lead to a distorted octahedral geometry, and the fact that in **2** no short Ru−Ru interaction is detectable as in compound **1** and PcRu.[7]

[Bis(3-fluoropyridine)phthalocyaninato]ruthenium(II) (3)

As in **2**, six shells are required to describe the EXAFS function (see Table 3 and Figure 7). Again, these are the four shells of the phthalocyanine macrocycle and, additionally, two nitrogen backscatterers at 2.57 Å, which only can be assigned to the ligand 3-fluoropyridine, because no ring atoms are located within this range. Furthermore, there are four carbon backscatterers at a distance of 3.41 Å, also from 3-fluoropyridine. In comparison to **2**, the distance of the ruthenium absorber and the nitrogen backscatterers of the ligand are not significantly different from each other.

Table 3. EXAFS-determined structural data of **3**

[a]		R [Å]	N	σ [Å]	ΔE_0 [eV]	Fit index
Ru−N	(A)	2.02±0.02	4.0	0.063±0.009	20.40	30.77
Ru−C	(A)	3.03±0.03	8.0	0.050±0.009		
Ru−N	(A)	3.23±0.03	4.0	0.080±0.009		
Ru−C	(A)	4.03±0.04	8.0	0.078±0.010		
Ru−N	(L)	2.57±0.03	2.0	0.098±0.011		
Ru−C	(L)	3.41±0.03	4.0	0.053±0.009		

[a] Absorber−backscatterer distance r, coordination number N and Debye-Waller factor σ with their calculated standard deviation. The letters in parentheses refer to the model in Figure 4 and indicate the molecule where the backscattering atom is located.

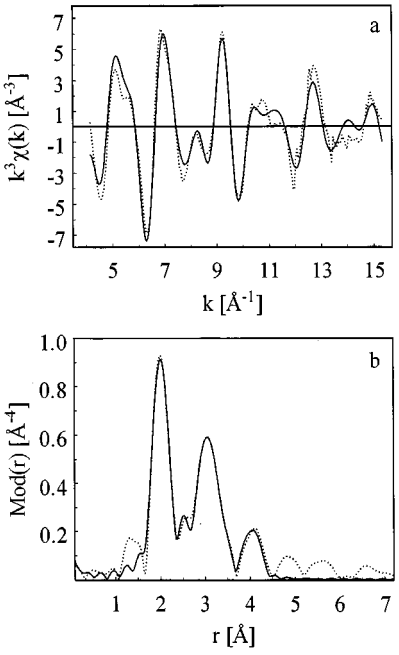

Figure 7. Experimental (dotted line) and calculated (solid line) $k^3 \cdot \chi(k)$ function (a) (k range: 4.15−15.35 Å^{-1}) and their Fourier transforms (b) of PcRu(3-Fpy)$_2$ (**3**) (see Table 3 for fitting parameters)

Table 4. EXAFS-determined structural data of **4**

[a]		R [Å]	N	σ [Å]	ΔE_0 [eV]	Fit index
Ru−N	(A)	2.03±0.02	4.0	0.062±0.009	20.70	25.46
Ru−C	(A)	3.04±0.03	8.0	0.051±0.009		
Ru−N	(A)	3.26±0.03	4.0	0.073±0.009		
Ru−C	(A)	4.03±0.04	8.0	0.073±0.010		
Ru−N	(L)	2.55±0.03	2.0	0.088±0.011		
Ru−C	(L)	3.42±0.02	4.0	0.049±0.009		

[a] Absorber−backscatterer distance r, coordination number N and Debye-Waller factor σ with their calculated standard deviation. The letters in parentheses refer to the model in Figure 4 and indicate the molecule where the backscattering atom is located.

[Bis(3-chloropyridine)octakis(pentyloxy)phthalocyaninato]-ruthenium(II) (4)

As with compounds **2** and **3**, at least six shells are necessary to describe the EXAFS function (see Table 4 and Figure 8). As the structure and the determined structural para-

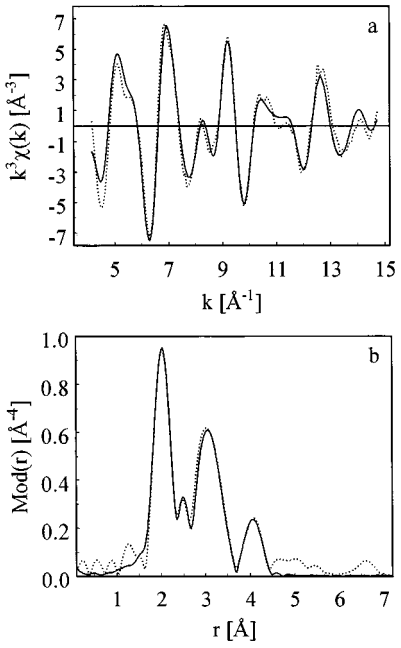

Figure 8. Experimental (dotted line) and calculated (solid line) $k^3 \cdot \chi(k)$ function (a) (k range: 3.50−14.80 Å^{-1}) and their Fourier transforms (b) of $(C_5H_{11}O)_8$PcRu(3-Clpy)$_2$ (**4**) (see Table 4 for fitting parameters)

meters of the PcRu complexes **2**, **3** and **4** are very similar, we refrain from further discussion of the structure of compound **4**.

Conclusion

It was possible to deduce structural models for tBu$_4$PcRu (**1**), tBu$_4$PcRu(3-Clpy)$_2$ (**2**), PcRu(3-Fpy)$_2$ (**3**) and $(C_5H_{11}O)_8$PcRu(3-Clpy)$_2$ (**4**) by EXAFS spectroscopy. The structure of tBu$_4$PcRu (**1**) is very similar to that of PcRu,[7] which forms a dimer. However, one has to take into consideration the four *tert*-butyl groups on both of the Pc rings, which could lead to severe steric hindrance in a dimeric structure of **1**. According to model considerations, the interaction between two *tert*-butyl groups, even in an eclipsed conformation, is not very high, e.g. if both rings adopt the C_{4h} structure, because the distance of the two coplanar Pc rings in **1** is 3.2 Å. This is also the case for the three additional structural isomers of tBu$_4$PcRu (**1**), namely the D_{2h}, C_{2v}, and the C_s isomers.[13] Less steric interaction of the *tert*-butyl groups will occur if the dimer (tBu$_4$PcRu)$_2$ is formed from two different structural isomers of tBu$_4$PcRu, e.g. if it is a mixture of the C_{4h} and the D_{2h} isomer. The Ru−Ru-distance in **1** and in the unsubstituted PcRu are quite similar.[7] This also points to a low steric interaction between the *tert*-butyl groups on both Pc rings in **1**. A dimeric structure for **1** is therefore quite feasible. Attempts to calculate the interactions between the *tert*-butyl groups by using the standard HyperChem program was not successful due to the large number of atoms in the dimer **1**.

Sixfold coordination of the ruthenium atom occurs in compounds in **2**, **3** and **4**. The ligands are axially located in an octahedral arrangement on both sides of the phthalocyanine macrocycle. The differences in the environment around the ruthenium centre between the PcRu with the 3-chloropyridine ligands and the 3-fluoropyridine ligands and the unsubstituted, tetra- and octa-substituted macrocycles are not very large, but it should be noted that the distances of the ruthenium atom to the nitrogen backscatterers of the pyridine ligands become smaller, and the distances of the ruthenium atom to the second nitrogen backscatterers of the phthalocyanine macrocycle increase in the sequence **3** > **4** > **2**. This could be interpreted as being due to nonplanar Pc rings in these compounds.

Experimental Section

General Remarks: ^{1}H, ^{13}C NMR: Bruker AC 250 (^{1}H: 250.133 MHz, ^{13}C: 62.902 MHz). − UV/Vis: Shimadzu UV−365. − FT IR: Bruker IFS 48. − Elemental analyses: Carlo Erba Elemental Analyser 1104, 1106. − MS: Varian Mat 711.

[Tetrakis(*tert*-butyl)phthalocyaninato]ruthenium(II) (tBu$_4$PcRu, 1): [Tetrakis(*tert*-butyl)phthalocyaninato]ruthenium(II) was prepared by thermal decomposition of bis(3-chloropyridine)[tetrakis(*tert*-butyl)phthalocyaninato]ruthenium(II) (**2**).[6a] − $C_{48}H_{48}N_8Ru$ (838.03): calcd. C 68.71, H 5.77, N 13.36; found C 68.00, H 5.99, N 13.01.

Bis(3-chloropyridine)[tetrakis(*tert*-butyl)phthalocyaninato]-ruthenium(II) (tBu$_4$PcRu(3-Clpy)$_2$, 2): Bis(3-chloropyridine)[tetrakis(*tert*-butyl)phthalocyaninato]ruthenium(II) (**2**) was prepared from 4-*tert*-butylphthalonitrile, $RuCl_3 \cdot 3H_2O$ and 3-chloropyridine according to the method described.[6a] − $C_{58}H_{56}Cl_2N_{10}Ru$ (1065.13): calcd. C 65.39, H 5.30, Cl 6.57, N 13.16; found C 65.39, H 6.06, Cl 6.57, N 13.19.

Phthalocyaninatoruthenium PcRu (**5**) was prepared according to the method described earlier.[4,5]

Bis(3-fluoropyridine)phthalocyaninatoruthenium (PcRu(3-Fpy)$_2$, 3): A mixture of (phthalocyaninato)ruthenium (**5**) (100 mg, 0.16 mmol), 3-fluoropyridine (31.5 mg, 0.32 mmol) and chloroform (10 mL) was heated at reflux for 6 h. The solution was poured into methanol/water (3:1) and the precipitate was centrifuged and dried. Purification was carried out by column chromatography (silica gel, chloroform, R_f = 0.65). After drying (50 °C, 0.01 Torr), pure **3** was obtained; yield 79 mg (61%). − $C_{42}H_{24}F_2N_{10}Ru$ (808.12): calcd. C 62.37, H 2.99, N 17.33; found C 62.51, H 3.02, N 16.97. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.21 (m, 2 H, 3-Clpy), 2.36 (m, 2 H, 3-Clpy), 5.24 (m, 2 H, 3-Clpy), 5.83 (m, 2 H, 3-Clpy), 7.97 (m, 8 H, Pc), 9.22 (m, 8 H, Pc). − IR (KBr): $\tilde{\nu}$ = 3111 cm^{-1} (vw), 3057 (vw), 2924 (vw), 1607 (w), 1582 (m), 1489 (vs), 1433 (m), 1414 (m), 1325 (m), 1288 (m), 1242 (m), 1238 (m), 1169 (vs), 1124 (vs), 1065 (m), 845 (m), 804 (m), 773 (m), 690 (w). − UV/Vis ($CHCl_3$): λ_{max} = 627 nm (Q), 573 sh, 402 sh, 369 sh, 312 (B).

Bis(3-chloropyridine)[1,4,8,11,15,18,22,25-octakis(pentyloxy)phthalocyaninato]ruthenium(II) (4): A mixture of 3,6-dipentyloxyphthalonitrile (3.0 g, 10 mmol), $RuCl_3 \cdot 3H_2O$ (650 mg, 2.5 mmol), 3-chloropyridine (570 mg, 5 mmol) and DBU (1 mL) in 2-ethoxyethanol (30 mL) was heated at reflux for 7 d under nitrogen, while monitoring the reaction by TLC (SiO_2/$CHCl_3$, R_f = 0.8). The solution was poured into methanol/water (3:1) and the precipitate was centrifuged and dried. The dry precipitate was subsequently subjected to Soxhlet extraction with methanol for 10 h.

Purification was carried out by column chromatography (silica gel, chloroform). After drying (60 °C, 0.01 Torr, 6 h) pure **4** was obtained; yield 485 mg (12.7%), green powder. − $C_{82}H_{104}Cl_2N_{10}O_8Ru$ (1529.77): calcd. C 64.37, H 6.86, Cl 4.58, N 9.16; found C 64.04, H 6.88, Cl 4.60, N 9.13. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 (t, J = 6.8 Hz, 24 H, CH_3), 1.56 (m, 32 H, 2 CH_2), 2.30 (m, 16 H, CH_2), 2.50 (m, 2 H, 3-Clpy), 2.51 (m, 2 H, 3-Clpy), 4.84 (t, J = 6.4 Hz 16 H, CH_2), 5.22 (m, 2 H, 3-Clpy), 6.10 (m, 2 H, 3-Clpy), 7.29 (s, 8 H, Pc). − ^{13}C NMR (250 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.7 (CH_2), 28.3 (CH_2), 29.3 (CH_2), 71.5 (−O−CH_2), 115.7 (Pc), 122.5 (3-Clpy), 129.6 (Pc), 130.5 (3-Clpy), 133.0 (3-Clpy), 143.3 (Pc), 148.5 (3-Clpy), 148.9 (3-Clpy), 150.4 (Pc). − IR (KBr): $\tilde{\nu}$ = 3097 cm^{-1} (vw), 3033 (vw), 2954 (s), 2927 (s), 1597 (m), 1498 (vs), 1465 (m), 1308 (m), 1283 (s), 1261 (s), 1219 (vs), 1111 (s), 1062 (s), 972 (w). − UV/Vis ($CHCl_3$): λ_{max} = 699 nm (Q), 630, 405, 312 (B). − MS (FAB, NBA); *m/z*: 1529.9 [M^+], 1303.8 [$M^+ - 2 \times$ 3-Clpy].

The EXAFS measurements of tBu$_4$PcRu (**1**), tBu$_4$PcRu(3-Clpy)$_2$ (**2**), PcRu(3-Fpy)$_2$ (**3**) and ($C_5H_{11}O$)$_8$PcRu(3-Clpy)$_2$ (**4**) were performed at the ruthenium K edge at 22118.0 eV at the beamline A1 at the *Hamburger Synchrotronstrahlungslabor* (HASYLAB) at DESY, Hamburg, at 25 °C, with an Si<311> double crystal monochromator under ambient conditions (5.4 GeV, beam current 100 mA). The tilt of the second monochromator crystal was set to 30% harmonic rejection. Energy resolution was estimated to be about 10 eV at the ruthenium K edge. Data were collected in transmission mode with ion chambers, which were continuously flushed with argon. Energy calibration was monitored with a 20-μm thick ruthenium metal foil. All measurements were performed under an inert gas. The samples were embedded in a polyethylene matrix, of which the thickness was adjusted to an absorption jump of Δμ = 1.5. Data were analysed with a program package specially developed for the analysis of amorphous samples.[14] The program AUTOBK of the University of Washington[15] was used for background removal and the program EXCURV92[16] for the evaluation of the XAFS functions. First, background absorption was removed from the experimental absorption spectrum by subtraction of a Victoreen-type polynomial. Then the background-subtracted spectrum was convoluted with a series of increasingly broader Gauss functions and the common intersection point of the convoluted spectra was taken as energy E_0.[14] To determine the smooth part of the spectrum, corrected for pre-edge absorption, a piecewise polynomial was used. It was adjusted in such a way that the low-R components of the resulting Fourier transform were minimal. After division of the background-subtracted spectrum by its smooth part, the photon energy was converted into a photoelectron wave number scale. The resulting EXAFS function was weighted with k^3. Data analysis in k space was performed according to the curved wave multiple scattering formalism of the program EXCURV92.[16] The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI was set to −4.00), the amplitude reduction factor AFAC was fixed at 0.8 and an overall energy shift ΔE_0 was assumed.

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