Structural Investigations of Oligomeric Axially Bridged Ruthenium Phthalocyanines by EXAFS Spectroscopy

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Keywords: EXAFS spectroscopy / Ruthenium / Phthalocyanines / Structure elucidation

To obtain more information about the structure of phthalocyaninatoruthenium compounds an EXAFS investigation was carried out on amorphous bisaxially bridged phthalocyaninatoruthenium(II) oligomers, $[PcRu(tz)]_n$ (**1**), $[PcRu(pyz)]_n$ (**2**) and $[PcRu(dib)]_n$ (**3**). Detailed structural models for the three compounds were deduced from the determined atomic distances around the metal center. A bisaxial structure of the ligands could be proven for all compounds and additionally, the structure parameters could be determined.

Introduction

In recent years phthalocyaninatoruthenium(II) 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 phthalocyaninatoruthenium(II) $(PcRu)_2$.[4] Later, we developed a convenient method for obtaining $(PcRu)_2$ by thermal decomposition of the corresponding bisisoquinoline or bis-3-chloropyridine complex $PcRu(L)_2$ (L = iqnl; 3-Clpy) at 250 or 270 °C,[5,6] respectively. This provides the basis for the preparation of axially bridged $[PcRu(L)]_n$ oligomers with bidentate bridging ligands L [e.g. L = pyrazine (pyz), *s*-tetrazine (tz), 1,4-diisocyanobenzene (dib)] as a new class of intrinsic semiconductors.[2,4]

An important condition for achieving electrical conductivity in phthalocyaninato compounds is the stacked arrangement of the macrocycles. Assuming a suitably small distance between cofacially arranged planar macrocycles possessing an extended π-electron system, electron delocalization by π-π overlap of the perpendicular orbitals in a stacked arrangement is possible. In particular, oxidation (or less frequently reductive doping) of the macrocycles generates charge carriers leading to semiconducting or conducting quasi-one-dimensional materials.

Phthalocyaninato compounds, however, do not crystallize in this stacked arrangement, except phthalocyaninatolead(II) (PcPb) in its monoclinic modification.[7] Metallophthalocyanines in general crystallize in an α- or β-modification (inclined stacked), which is not favorable for π-orbital overlap and thus for the formation of a conducting band.

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Some years ago a route was developed to stacked arrangements of phthalocyaninato transition metal compounds which lead to coordination oligomers and polymers where the macrocycle, the central metal atom and the bridging ligand can be varied systematically. The stacking is achieved by connecting the central transition metal atoms of the macrocycle with bidentate bridging ligands L bisaxially. Such bridged macrocyclic transition metal compounds $[MacM(L)]_n$ have been synthesized and investigated in detail with respect to their physical properties.[8,9] The bridging ligands L are linear π-electron-containing organic molecules, for example pyrazine, 1,4-diisocyanobenzene or substituted 1,4-diisocyanobenzenes, *s*-tetrazine or substituted tetrazines, and others. Many of the bridged macrocyclic metal complexes $[MacM(L)]_n$ (“shish-kebab polymers”) can be prepared in high yields and high purity by treating the metallomacrocycle MacM with the pure ligand or with the ligand in an appropriate solvent. The bridged structure has been confirmed for many compounds using a variety of physical methods[8] including detailed IR investigations,[10] Mössbauer spectroscopy,[11] ^1H and ^{13}C NMR spectroscopy[12] and scanning tunneling microscopy (STM).[13]

$(PcRu)_2$ reacts easily with ligands L such as pyrazine, *s*-tetrazine, 1,4-diisocyanobenzene and others to form the corresponding monomers $PcRu(L)_2$, and under somewhat different conditions to form the bridged systems $[PcRu(L)]_n$.[4,14] Although the monomeric complexes $PcM(L)_2$ (L = pyz, tz, dib; M = Fe, Ru, Os) are all insulators, it can be seen that the ligand (L) has a significant effect on the conductivity of the bridged complexes $[PcM(L)]_n$: as 1,4-diazabicyclo[2.2.2]octane (dabco) is a ligand containing no π-orbitals to interact with the metallomacrocycle the $[PcM(dabco)]_n$ complexes are also insulators,[2] whereas an increase in electrical conductivity is observed for the pyrazine- and 1,4-diisocyanobenzene-bridged compounds. $[PcRu(pyz)]_n$ (**2**) and $[PcRu(dib)]_n$ (**3**) exhibit electrical conductivities ($\sigma_{RT} = 1 \times 10^{-7}$ S cm^{-1} and σ_{RT} =

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2×10^{-6} S cm^{-1})[4,15] in the low semiconducting region. However, by changing the bridging ligand to *s*-tetrazine or its derivatives the conductivity increases by three to five orders of magnitude without external oxidative doping.[2,16] With *s*-tetrazine as the ligand in $[PcRu(tz)]_n$ (**3**), a powder conductivity of 0.01 S cm^{-1} can be achieved.

Structural investigations on oligomeric phthalocyaninatoruthenium(II) compounds with EXAFS or LAXS spectroscopy have only been performed on oxygen-containing materials up to now.[3] Extended X-ray absorption fine structure (EXAFS) has been considered to be a powerful technique for determining the local atomic environment of a specific atom without regard to the state of the sample. An analysis of the EXAFS provides information on the bond length, the coordination number, the "Debye−Waller"-like factor, and the nature of the scattering atoms surrounding an excited atom.[17,18] In this paper, we have studied (μ-*s*-tetrazine)phthalocyaninatoruthenium(II) (**1**), (μ-pyrazine)phthalocyaninatoruthenium(II) (**2**) and (μ-1,4-diisocyanobenzene)phthalocyaninatoruthenium(II) (**3**) as amorphous solids by transmission EXAFS spectroscopy.

Results and Discussion

(μ-*s*-Tetrazine)phthalocyaninatoruthenium(II) (1)

In the Fourier transforms (see Figure 1b and 1d), several coordination shells are visible. In fitting the EXAFS function to the experiment we fixed the coordination numbers to the known values of the phthalocyanine molecule. Furthermore, the four shells of the phthalocyanine macrocycle were only fitted independently in such a way that the determined distances led to meaningful interatomic distances in the macrocycle itself. Taking these considerations into account the number of parameters decreases from 12 to 9 and is clearly less than the number of independent data points (22).[19]

Five backscatterers are necessary for a good fit of the EXAFS function (see Figure 1c, 1d and Table 1). These are the four backscatterers of the phthalocyanine macrocycle and one nitrogen backscatterer, which can be traced back to the bridging ligand *s*-tetrazine at a distance of 2.22 Å. Without this backscatterer the fit worsens significantly to

Table 1. EXAFS-determined structural data of **1**[a]

1	*N*	R^4, Å	σ^4, Å	R^5, Å	σ^5, Å
$Ru-N_{Indol}$	4	2.02±0.02	0.068±0.011	2.02±0.02	0.058±0.013
Ru−C	8	3.02±0.03	0.081±0.014	3.04±0.03	0.076±0.016
$Ru-N_{Aza}$	4	3.22±0.03	0.088±0.009	3.27±0.03	0.088±0.016
Ru−C	8	3.97±0.04	0.095±0.019	3.98±0.04	0.080±0.014
$Ru-N_{tz}$	2			2.22±0.02	0.075±0.009

[a] Absorber−backscatterer distance *r*, coordination number *N* and Debye−Waller factor σ with their calculated standard deviation. The simulations with four and five backscatterers are marked by the superscripts 4 and 5. The ΔE_0 shift of **1** of EXCURV92 is 19.03 eV and the *R*-factors are 35.8[4] and 28.2[5].

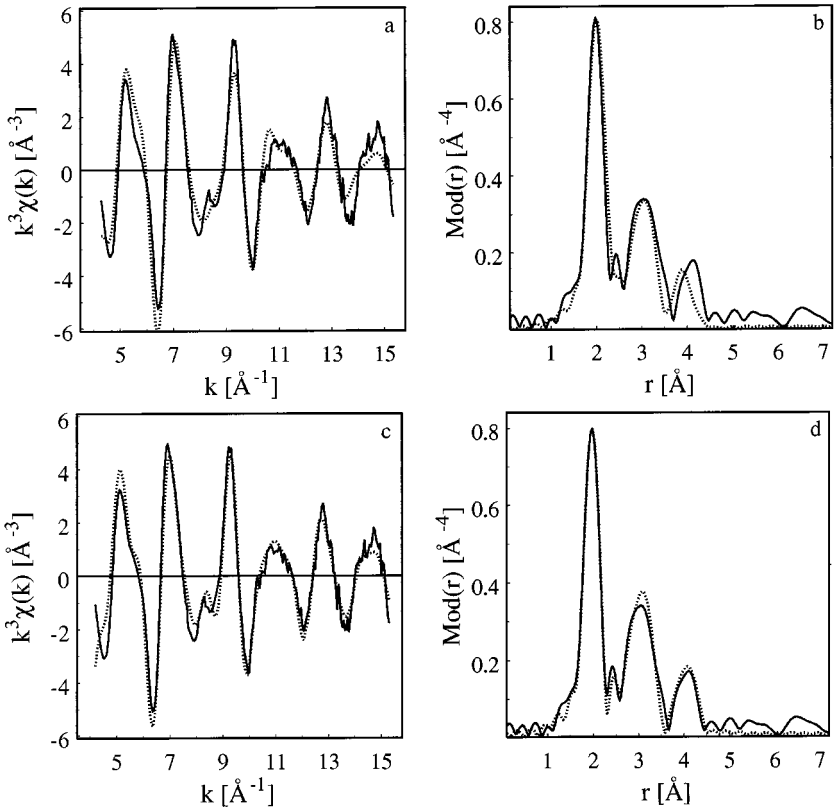

Figure 1. Experimental (solid line) and calculated (dotted line) Ru−K $k^3 \cdot \chi(k)$ functions (a, c) and their corresponding Fourier transforms without phase correction (b, d) of **1** (*k* range: 3.45−15.45 Å^{-1}); simulation with four (a, b) and five (c, d) backscatterers; the corresponding structural data are given in Table 1

about 21%. The difference of the fit with four and five backscatterers can be compared in Figure 1a and 1b (four backscatterers) and Figure 1c and 1d (five backscatterers). The resulting model of **1** with the determined distances can be seen in Figure 2a.

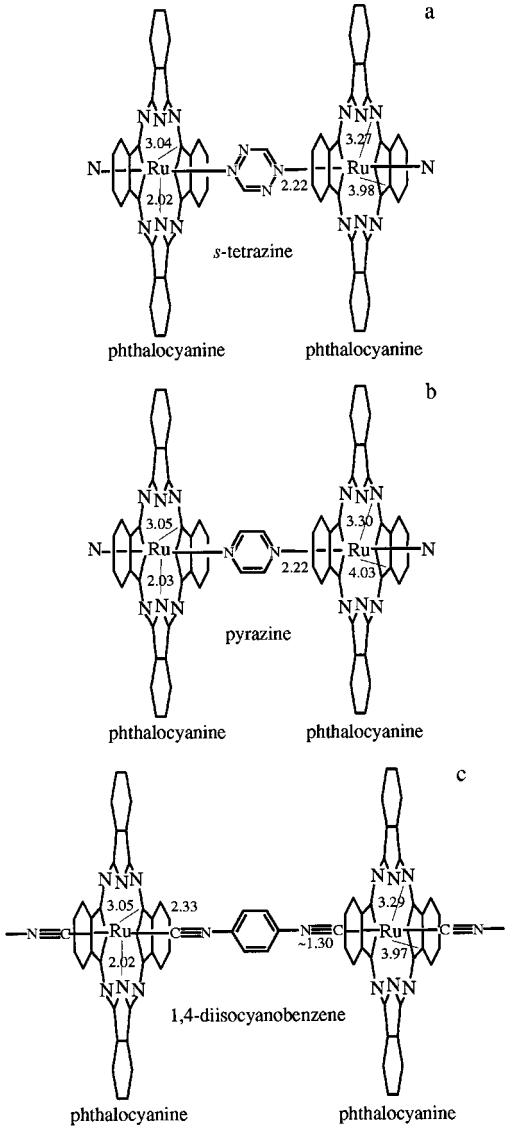

Figure 2. Determined distances and proposed structures of **1** (a), **2** (b) and **3** (c)

Without any knowledge of the structure, one would expect the ruthenium atom to be 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 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.

Since only single scattering contributes to the EXAFS function, we are forced to assume that the ruthenium atom

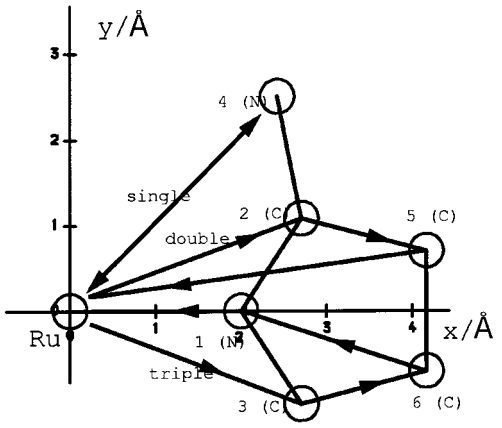

Figure 3. Defined multiple scattering unit illustrating single, double and triple scattering paths; for reasons of clarity the axially coordinated ligand atom is not drawn, but included in our calculations

is not positioned in the plane of the ring, the ring 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 astonishing result that the amount of multiple scattering does not depend very strongly on the out-of-plane position of the ruthenium atom. The contribution of the multiple scattering almost vanishes only when the displacement amounts to 1.75 Å. 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 that the possible displacement of the ruthenium atom — if it exists — plays only a minor role. From the determined distances, it is not possible to make any structural statements concerning the nonplanarity of the macrocycle.

(μ-Pyrazine)phthalocyaninatoruthenium(II) (2)

For a good simulation of the EXAFS function of compound **2**, at least five shells are necessary (see Table 2 and Figure 4). These are the four shells of the phthalocyanine macrocycle and an additional nitrogen backscatterer at 2.22 Å, which can only be assigned to the ligand pyrazine as there are no ring atoms located in that distance range. The fit index decreases to about 9% if we take five shells of

Table 2. EXAFS-determined structural data of **2**[a]

2	N	R^4, Å	σ^4, Å	R^5, Å	σ^5, Å
$Ru-N_{Indol}$	4	2.04±0.02	0.074±0.009	2.03±0.02	0.066±0.010
Ru−C	8	3.05±0.03	0.073±0.014	3.05±0.03	0.071±0.016
$Ru-N_{Aza}$	4	3.31±0.03	0.088±0.012	3.30±0.03	0.087±0.012
Ru−C	8	4.03±0.04	0.087±0.022	4.03±0.04	0.084±0.021
$Ru-N_{pyz}$	2			2.22±0.03	0.099±0.023

[a] Absorber−backscatterer distance r, coordination number N and Debye−Waller factor σ with their calculated standard deviation. The simulations with four and five backscatterers are marked by the superscripts 4 and 5. The ΔE_0 shift of **2** is 19.60 eV and the R-factors are 38.9[4] and 35.4[5].

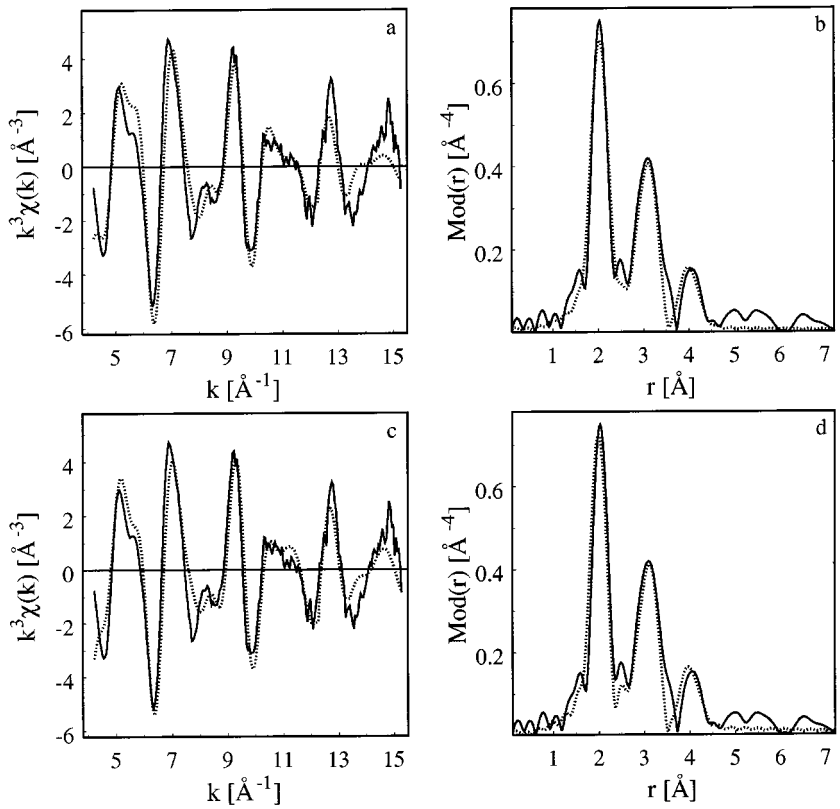

Figure 4. Experimental (solid line) and calculated (dotted line) Ru−K $k^3 \cdot \chi(k)$ functions (a, c) and their corresponding Fourier transforms without phase correction (b, d) of **2** (k range: 3.45−15.45 Å^{-1}); simulation with four (a, b) and five (c, d) backscatterers; the corresponding structural data are given in Table 2

the phthalocyanine macrocycle instead of four into account (compare Figure 4a, 4b and 4c, 4d).

If we make the simplified assumption that the four nitrogen atoms of the phthalocyanine macrocycle that form the first coordination shell lie in a plane, the displacement of the ruthenium atom can be explained in the following way. From crystallographic data we know that the metal−nitrogen distance of planar systems, for example in phthalocyaninatomanganese(tetracyanoethenide), is typically 1.97 ± 0.3 Å.[20−22] As a 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 ± 0.3 Å outside the plane of the macrocycle (see Figure 2). It should be noted that this triangulation depends critically on both the measured Ru−N distance and the assumed N-center distance. It is only given here to get a rough estimation of the amount of the possible displacement. The resulting model of **2** with the determined distances can be seen in Figure 2b.

(μ-1,4-Diisocyanobenzene)phthalocyaninatoruthenium(II) (3)

As in **1**, five shells are required to describe the EXAFS function (see Table 3 and Figure 5). Again, these are the four shells of the phthalocyanine macrocycle and one additional carbon backscatterer at 2.33 Å, which can only be assigned to the ligand 1,4-diisocyanobenzene as in that distance range no ring atoms are located. The fit worsens drastically (nearly 40%) if we do not take this fifth carbon backscatterer into account (compare Figure 5a and 5b with 5c and 5d). Further backscatterers could not be found by EXAFS spectroscopy. The next distance to the nitrogen from the 1,4-diisocyanobenzene should be about 1.3 Å further away than the carbon backscatterer (at about 3.6 Å). A fitting with this backscatterer in this distance range does not increase the agreement of the experimental EXAFS function compared to the fitted function. The resulting model of **3** with the determined distances can be seen in Figure 2c.

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

3	N	R^4, Å	σ^4, Å	R^5, Å	σ^5, Å
Ru−N_{Indol}	4	2.02±0.02	0.105±0.021	2.03±0.02	0.094±0.020
Ru−C	8	3.04±0.03	0.101±0.023	3.05±0.03	0.092±0.023
Ru−N_{Aza}	4	3.30±0.03	0.069±0.012	3.29±0.03	0.072±0.014
Ru−C	8	3.99±0.04	0.095±0.019	3.97±0.04	0.096±0.020
Ru−C_{dib}	2			2.33±0.03	0.071±0.014

[a] Absorber−backscatterer distance r, coordination number N and Debye−Waller factor σ with their calculated standard deviation. The simulations with four and five backscatterers are marked by the superscripts 4 and 5. The ΔE_0 shift of **3** is 19.05 eV and the R-factors are 49.4[4] and 30.4[5].

Conclusion

It was possible to deduce detailed structural models for (μ-*s*-tetrazine)phthalocyaninatoruthenium(II) (**1**), (μ-pyraz-

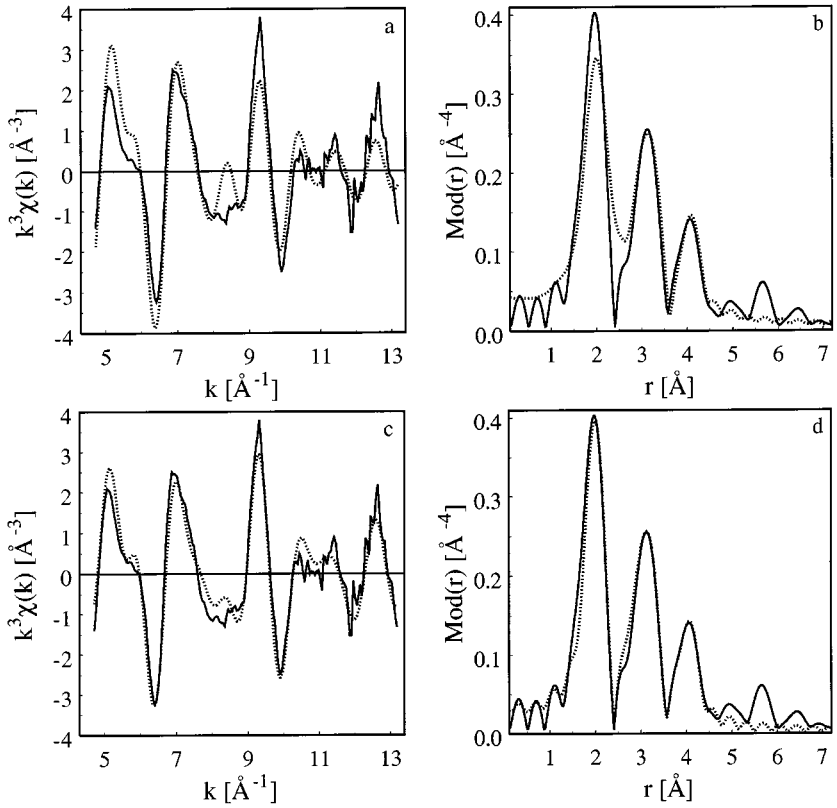

Figure 5. Experimental (solid line) and calculated (dotted line) Ru−K k^3·$\chi(k)$-functions (a, c) and their corresponding Fourier transforms without phase correction (b, d) of **3** (k range: 3.45−13.25 Å^{-1}); simulation with four (a, b) and five (c, d) backscatterers; the corresponding structural data are given in Table 3

ine)phthalocyaninatoruthenium(II) (**2**) and (μ-1,4-diisocyanobenzene)phthalocyaninatoruthenium(II) (**3**) by EXAFS spectroscopy. A sixfold coordination of the ruthenium atom exists in the investigated compounds, where the bridging ligands are located axially in an octahedral arrangement on both sides of the phthalocyanine macrocycle. The differences in the environment around the ruthenium center between the compounds **1**, **2** and **3** are not significant.

Experimental Section

^{1}H NMR: Bruker ARX 250 (250.133 MHz), as internal standard [D$_5$]pyridine was used. − UV/Vis Shimadzu UV−365. − Elemental analyses: Carlo Erba Elemental Analyzer 1104, 1106. Due to the formation of ruthenium nitride and carbide, only hydrogen values were determined by elemental analysis for the oligomeric phthalocyaninatoruthenium complexes **1**−**3**.

Starting Materials and General Methods: Pyrazine was commercially available. 1,4-Diisocyanobenzene[23] and *s*-tetrazine[24] were prepared according to known procedures. Phthalocyaninatoruthenium was prepared according to the method described previously.[5]

(μ-*s*-Tetrazine)phthalocyaninatoruthenium(II) (1): A mixture of phthalocyaninatoruthenium (**1**) (100 mg, 0.16 mmol), *s*-tetrazine (15 mg, 0.18 mmol), and dry tetrahydrofuran (10 mL) was refluxed under an inert gas atmosphere for 6 days. After cooling to room temperature, the reaction mixture was centrifuged. The collected solid was washed several times with acetone and then dried in vacuo at 70 °C. Yield: 87 mg (78%), blue-black powder.

$[C_{34}H_{18}N_{12}Ru]_n$ ($[695.67]_n$): calcd. H 3.1; found H 3.1. − ^{1}H NMR (250 MHz, [D$_5$]pyridine, 25 °C): δ = 7.78−8.13 (m, 1 H, Pc-H$_a$), 8.75−9.44 (m, 1 H, Pc-H$_b$). − UV/Vis (chlorobenzene): λ_{max} = 642, 583 nm.

(μ-Pyrazine)phthalocyaninatoruthenium(II) (2): A mixture of phthalocyaninatoruthenium (100 mg, 0.16 mmol), pyrazine (15 mg, 0.19 mmol), and dry tetrahydrofuran (10 mL) was refluxed under an inert gas atmosphere for 6 days. After cooling to room temperature, the reaction mixture was centrifuged. The collected solid was washed several times with acetone and dried in vacuo at 70 °C. Yield: 67 mg (60%), dark blue powder.

$[C_{36}H_{20}N_{10}Ru]_n$ ($[693.69]_n$): calcd. H 2.9; found H 2.9. − ^{1}H NMR(250 MHz, [D$_5$]pyridine, 25 °C): δ = 5.67 (m, 1H; pyrazine), 7.86−8.01 (m, 4 H, Pc-H$_a$), 9.44−9.55 (m, 4 H, Pc-H$_b$). − UV/Vis (chlorobenzene): λ_{max} = 639, 585 nm.

(μ-1,4-Diisocyanobenzene)phthalocyaninatoruthenium(II) (3): A mixture of phthalocyaninatoruthenium (**1**) (100 mg, 0.16 mmol), 1,4-diisocyanobenzene (22 mg, 0.17 mmol), and dry tetrahydrofuran (10 mL) was refluxed under an inert gas atmosphere for 6 days. After cooling to room temperature, the reaction mixture was centrifuged. The collected solid was washed several times with acetone and then dried in vacuo at 70 °C. Yield: 91 mg (75%), blue-black powder.

$[C_{40}H_{20}N_{10}Ru]_n$ ($[742.09]_n$): calcd. H 2.8; found H 2.8. − ^{1}H NMR (250 MHz, [D$_5$]pyridine, 25 °C): δ = 3.6−3.7 (m, 4 H, 1,4-diisocyanobenzene), 7.88−8.06 (m, 8 H, Pc-H$_a$), 9.36−9.57 (m, 8 H, Pc-H$_b$). − UV/Vis (chlorobenzene): λ_{max} = 640, 582 nm.

EXAFS Measurements: The EXAFS measurements of the oligomeric phthalocyaninatoruthenium complexes **1**−**3** were performed

at the ruthenium K edge at 22118 eV, at the beamline A1, at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY, Hamburg, with a 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 atmosphere. The samples were embedded in a polyethylene matrix, whose thickness was adjusted to an absorption jump of $\mu = 1.5$. First, background absorption was removed from the experimental absorption spectrum by subtraction of a Victoreen-type polynomial. Then, the spectrum with background subtracted was convoluted with a series of increasingly broader Gaussian functions and the common intersection point of the convoluted spectra was taken as energy E_0.[25,26] To determine the smooth part of the spectrum, corrected for pre-edge absorption, a piecewise polynomial was used. It was adjusted in such a manner 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 wavenumber 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 with the XALPHA phase and amplitude functions.[27] 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 (E_0) was assumed.

Acknowledgments

We wish to thank HASYLAB (Hamburg) for kind support of synchrotron radiation and the Fonds der Chemischen Industrie for generous financial support. This work has been supported by the DFG (Grant No. Li 154/41−4).

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Received July 17, 2000
[I00279]