Structural Investigations of Ruthenium Phthalocyanines with EXAFS Spectroscopy

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To obtain a more detailed insight into the structure of PcRu **(1)**, an EXAFS investigation has been carried out on amorphous PcRu and compared with the bisubstituted PcRu(*n*-BuNH$_2$)$_2$ (**2**). From the obtained atomic distances around the metal center, it was possible to deduce detailed structural models for both compounds. For **1**, the dimeric structure was confirmed; for **2**, the EXAFS measurements led to an unusual structure in which both *n*-butylamine groups are located on one side of the PcRu ring.

Introduction

A considerable amount of research has been focused in recent years on the preparations, the chemistry, and the structure determinations of ruthenium phthalocyanines.[1−3] Some years ago we reported for the first time the synthesis of pure ruthenium phthalocyanine, PcRu, by thermal decomposition of the complex PcRu(DMSO)$_2$.[4] The synthesis of PcRu using this route however was improved by decomposition of the corresponding bis(pyridine) PcRu(py)$_2$ or bis(isoquinoline) PcRu(iqnl)$_2$ complexes, respectively.[5] The readily available PcRu(iqnl)$_2$ decomposes at 250 °C with the formation of analytically pure PcRu.[5] This synthetic route provided the basis for the preparation of novel bridged PcRu oligomers [PcRu(L)]$_n$ with L = pyz (pyrazine), dib (1,4-diisocyanobenzene), tz (*s*-tetrazine), and others as a new class of intrinsic semiconductors.[2]

PcRu—like most other metallophthalocyanines—is practically insoluble in organic solvents. Its solubility can be increased, however, by introducing alkyl or alkoxy groups into the peripheral positions of the Pc macrocycle. (Tetra-*tert*-butylphthalocyaninato)ruthenium (*t*-Bu$_4$PcRu)[6a] and several (octaalkoxyphthalocyaninato)ruthenium compounds[5,6b,c] are examples of soluble ruthenium phthalocyanines. Recently, (2,3-naphthocyaninato)ruthenium (2,3-NcRu)[7] and (tetra-*tert*-butyl-2,3-naphthocyaninato)ruthenium (*t*-Bu$_4$-2,3-NcRu)[6a] were also prepared.

A key problem concerning the exact structure determination of PcRu is the fact that PcRu **(1)** could be obtained so far only as an amorphous or microcrystalline material. Ercolani et al.[3] examined PcRu by large-angle X-ray scattering (LAXS) and deduced a dimeric structure (PcRu)$_2$ with a short Ru−Ru contact of 2.40 Å from the obtained data. (PcRu)$_2$ is paramagnetic with a temperature-dependent magnetic moment of 2.54 μ_B (at room temperature), indicating additionally the presence of a Ru−Ru double bond. Comparable magnetic data were found for *t*-Bu$_4$-PcRu[6a] (1.6 μ_B at 300 K) and 2,3-NcRu[7] (1.58 μ_B at room temperature), which also suggests a dimeric structure for both compounds.

Using LAXS for the structure determination of PcRu has the disadvantage that the interesting local environment around the ruthenium atom could only be determined indirectly. EXAFS spectroscopy, however, allows a direct and very exact measurement of the atomic distances which are located around the central Ru atom. The aim of our study is to investigate the structure of amorphous PcRu **(1)** and compare it with that of the bisubstituted monomer PcRu(*n*-BuNH$_2$)$_2$ **(2)** and to verify the earlier reported short Ru−Ru double bond in **1** using precise spectroscopic measurements. PcRu(*n*-BuNH$_2$)$_2$ **(2)** was also selected as an EXAFS spectroscopic model because the short Ru−Ru contact should be absent due to the ligand attachment.

Experimental Section

(Phthalocyaninato)ruthenium (1). (Phthalocyaninato)ruthenium (**1**) was prepared according to the method described earlier.[5]

Bis(*n*-butylamine)(phthalocyaninato)ruthenium (2). A mixture of (phthalocyaninato)ruthenium (**1**) (100 mg, 0.16 mmol), *n*-butylamine (23.4 mg, 0.32 mmol), and 10 mL of chloroform was refluxed 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 **2** was obtained: yield 70 mg (58%): purple powder. Anal. Calcd for $C_{40}H_{32}N_{10}Ru$ ($M_r = 759.88$): C, 63.23; H, 5.04; N, 18.43. Found: C, 63.56; H, 5.16; N, 18.10. ^{1}H NMR (250 MHz, CDCl$_3$): δ 9.12 (m, 8H, Pc), 7.88 (m, 8H, Pc), −0.27 (t, 6H, CH$_3$), −0.56 (m, 4H, CH$_2$), −1.21 (m, 4H, CH$_2$), −2.41 (m, 4H, CH$_2$), −5.95 (t, 4H, NH$_2$). ^{13}C NMR (250 MHz, CDCl$_3$): δ 143.9, 140.7, 127.8, 121.2, 39.1, 31.4, 17.8, 12.3. IR (KBr; cm^{-1}): 3231 vw, 3049 vw, 2956 vw, 2925 vw, 2871 vw, 1487 s, 1413 s, 1323 m, 1289 s, 1168, vs, 1122 vs, 1066 s, 754 m, 736 vs. UV/vis (CDCl$_3$), λ_{max} (nm): 628, 576 sh, 439 sh, 382, 314. MS (FD, CH$_2$Cl$_2$): *m*/*e* 760.1 (M$^+$).

The EXAFS measurements of PcRu (**1**) and PcRu(*n*-BuNH$_2$)$_2$ (**2**) were performed at the ruthenium K-edge at 22118.0 eV at the RÖMO II beamline at the Hamburger Synchrotronstrahlungslabor (HASYLAB),

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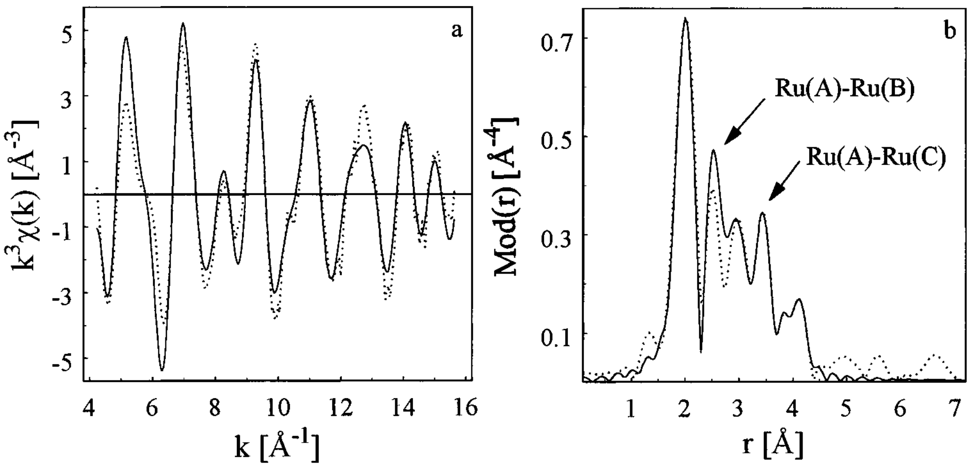

Figure 1. Experimental (dotted line) and calculated (solid line) $k^3\,\chi(k)$ functions (a) (k range: 3.45−15.50 Å^{-1}) and their Fourier transforms (b) for PcRu (**1**) (see Table 1 for fit parameters).

DESY, Hamburg, at 25 °C, with a Si⟨311⟩ double-crystal monochromator under ambient conditions (5.4 GeV, beam current 50 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 the transmission mode with ion chambers. The first ion chamber, monitoring I_0, with a length of 15 cm was continuously flushed with a mixture of 45% nitrogen and 55% argon. The second and third ion chambers, recording I_1 and I_2, respectively, with a length of 30 cm were flushed with 100% argon. The filling of the ion chambers was chosen in such a way that about 10% of the incident X-rays were absorbed in the first ion chamber and about 80% in the sample itself.[8] 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 of a mass ratio sample to polyethylene of 1.66 (**1**) and 2.00 (**2**).

Data were analyzed with a program package esspecially developed for the requirements of amorphous samples.[9] The program AUTOBK of the University of Washington[10] was used for background removal, and the program EXCURV90[11] was used for evaluation of the XAFS functions. In the first step, 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.[9] To determine the smooth part of the background-subtracted spectrum, a piecewise polynominal was used. It was adjusted in such a way that the low-R components of the resulting Fourier transform were optimized. 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 EXCURV90.[11] 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 introduced to receive the best fit of the data.

Table 1. EXAFS-Determined Structural Data: Absorber−Backscatterer Distance[a]

	r, Å	N	σ, Å	ΔE_0, eV	fit index
Ru−N (A)	2.03 ± 0.01	4.0	0.069 ± 0.014	23.01	31.42
Ru−C (A)	3.03 ± 0.01	8.0	0.079 ± 0.020		
Ru−N (A)	3.21 ± 0.01	4.0	0.056 ± 0.025		
Ru−C (A)	4.03 ± 0.01	8.0	0.074 ± 0.029		
Ru−Ru (B)	2.41 ± 0.01	1.0	0.089 ± 0.017		
Ru−N (B)	3.37 ± 0.02	4.0	0.069 ± 0.036		
Ru−Ru (C)	3.52 ± 0.01	1.0	0.074 ± 0.025		
Ru−N (C)	3.84 ± 0.02	4.0	0.059 ± 0.029		

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

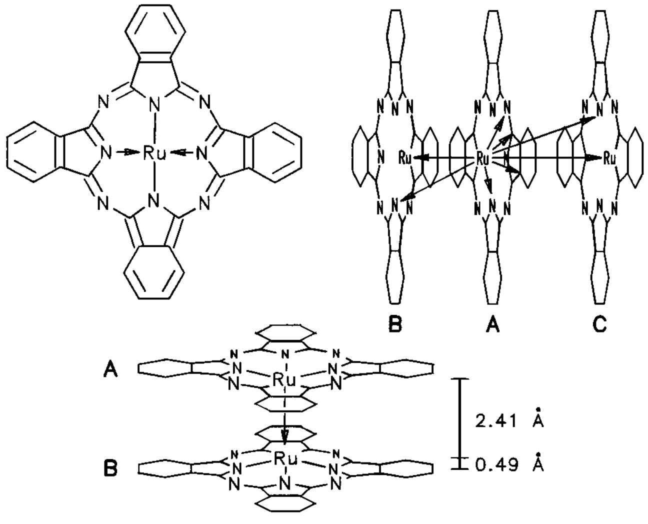

Figure 2. Structural model of PcRu (**1**) including the assignment of the determined distances to the corresponding atoms (see Table 1). For reasons of clarity in the right drawing, not all nitrogen atoms are shown.

Results and Discussion

(Phthalocyaninato)ruthenium (1). As can be seen in the Fourier transform (see Figure 1b), there are several well-pronounced shells. In fitting the EXAFS function, we are forced to describe it by at least eight shells. The number of eight shells in the fitting procedure seems to be very high, but it is not for two reasons. First, the coordination numbers were fixed on the known values of the phthalocyanine molecule. Second, the four shells marked with (A) in Table 1 for the phthalocyanine molecule (see Figure 2) cannot be fitted independently owing to the structure of the molecule, so that the number of parameters is much less than the number of independent data points.[12]

Without any preknowledge of the structure, one would expect the ruthenium atom to be located in the plane of the phthalo-

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Table 2. EXAFS-Determined Structural Data: Absorber–Backscatterer Distance[a]

	r, Å	*N*	*σ*, Å	ΔE_0, eV	fit index
Ru–N (A)	1.99 ± 0.01	4.0	0.063 ± 0.016	25.97	36.24
Ru–C (A)	3.00 ± 0.01	8.0	0.074 ± 0.021		
Ru–N (A)	3.26 ± 0.01	4.0	0.071 ± 0.026		
Ru–C (A)	3.92 ± 0.01	8.0	0.081 ± 0.029		
Ru–N (L)	2.52 ± 0.01	2.0	0.100 ± 0.035		

[a] *r*, coordination number *N*, and Debye–Waller factor *σ* with their calculated standard deviations. The letters in parentheses refer to the model in Figure 4 and indicate the molecule where the backscattering atom is located.

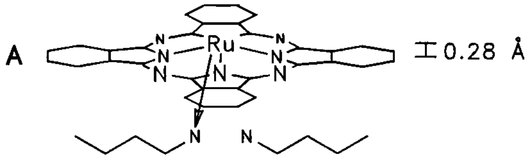

Figure 3. Structural model of PcRu(n-BuNH$_2$)$_2$ (**2**) including the assignment of the determined distances to the corresponding atoms (five-shell model; see Table 2).

Table 3. EXAFS-Determined Structural Data: Absorber–Backscatterer Distance[a]

	r, Å	*N*	*σ*, Å	ΔE_0, eV	fit index
Ru–N (A)	1.99 ± 0.01	4.0	0.063 ± 0.016	25.97	29.80
Ru–C (A)	3.00 ± 0.01	8.0	0.074 ± 0.021		
Ru–N (A)	3.26 ± 0.01	4.0	0.071 ± 0.026		
Ru–C (A)	3.92 ± 0.01	8.0	0.081 ± 0.029		
Ru–N (L)	2.52 ± 0.01	2.0	0.100 ± 0.035		
Ru–N (L)	3.71 ± 0.02	2.0	0.059 ± 0.032		
Ru–Ru (B)	4.14 ± 0.01	1.0	0.077 ± 0.038		

[a] *r*, coordination number *N*, and Debye–Waller factor *σ* with their calculated standard deviations. The letters in parentheses refer to the model in Figure 6 and indicate the molecule where the backscattering atom is located.

cyanine ring. If it is so, a considerable amount of multiple scattering should contribute to the EXAFS function. This is, however, not the case and indicates that the ruthenium atom is not positioned in the plane of the ring, or the ring itself is not planar, or both cases have to be assumed. Further evidence for this fact is the long Ru–N distance of the first shell of 2.03 Å (see Table 1). From crystallographic data,[13,14] we know that the metal–nitrogen distance for in-plane systems, e.g. in (phthalocyaninato)manganese tetracyanoethenide, is 1.97 Å or less. If we assume a planar ring system and a Ru–N distance of at least 1.97 Å, we can roughly calculate that the ruthenium atom is 0.49 Å out of the plane of the macrocycle (see Figure 2). Ercolani et al.[3] determined a distance of 0.41 Å for their model.

Besides the expected four shells of the phthalocyanine molecule, a significant improvement (41.6%) in the fit index can be obtained, if we assume a Ru–Ru distance of 2.41 Å in the simulation of the spectrum (see Table 1). This result is in very good agreement with the data of Ercolani et al.,[3] who determined 2.40 Å for the Ru–Ru double bond. Additionally, we found a second Ru–Ru distance at 3.52 Å (see Figure 2 and Table 1). This indicates that the next-neighboring-phthalocyanine molecule marked with (C) in Table 1 is located at a shorter distance than Ercolani et al. (4.32 Å) have predicted. Furthermore, we found four nitrogen backscatterers at 3.37 Å and four nitrogen backscatterers at 3.84 Å. These distances can be assigned to the corresponding atoms in macrocycles B and C, respectively.

Bis(n-butylamine)(phthalocyaninato)ruthenium (2). To describe the EXAFS function of **2** with a minimal basis set, at least five shells are necessary (see Table 2). These are the expected four shells of the phthalocyanine molecule and additionally two nitrogen backscatters at 2.52 Å, which only can be assigned to the ligand *n*-butylamine, because in that distance range no ring atoms are located. In comparison with those of compound **1**, all distances of the phthalocyanine molecule are shorter and no short Ru–Ru distance has been found. Coordination of the ligand *n*-butylamine should prevent the formation of a dimeric phthalocyanine unit coupled over a Ru–Ru double bond.

Surprisingly, the ruthenium–ligand distance in PcRu(n-BuNH$_2$)$_2$ **(2)** is unexpectedly long and only *one* distance is found. As for compound **1**, we know that the ruthenium atom is at least located at 0.28 Å (with the given assumptions) out of the plane of the macrocycle. The only explanation for these facts is that the ligand molecules are coordinated on one side of the phthalocyanine molecule and at a position that is opposite to the out-of-plane location of the ruthenium atom (see Figure 3). Otherwise a shorter Ru–N (L) distance would be expected.

As one can see in Figure 4, the agreement between the experimental and the calculated EXAFS function with five shells is not absolutely perfect. Especially, the peak at 4.1 Å in the Fourier transform is not well described with the eight carbon backscatterers of the phthalocyanine molecule. A significant improvement (17.8%) in the fit index can be obtained if we introduce further Ru–N and Ru–Ru distances at 3.71 and 4.13 Å, respectively (see Table 3 and Figure 5). From the determined

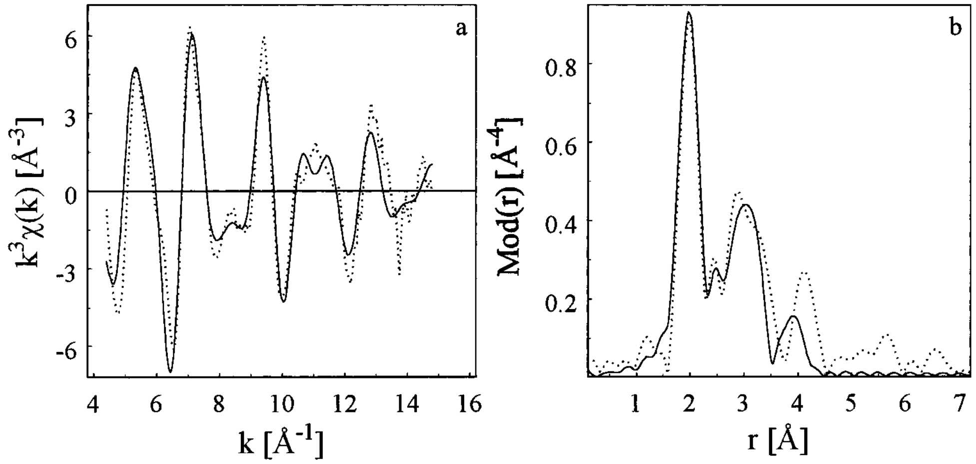

Figure 4. Experimental (dotted line) and calculated (solid line) $k^3\chi(k)$ functions (a) (k range: 3.45–14.45 Å^{-1}) and their Fourier transforms (b) for PcRu(n-BuNH$_2$)$_2$ (**2**) (five-shell model; see Table 2 for fit parameters).

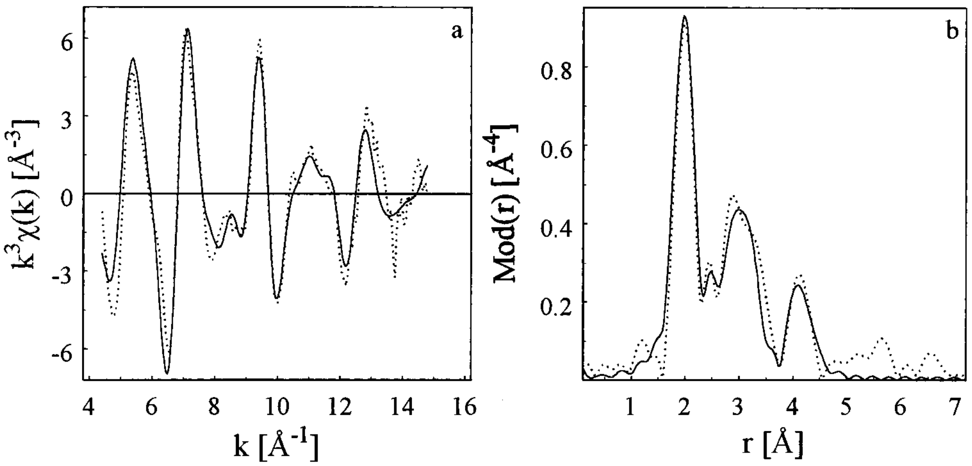

Figure 5. Experimental (dotted line) and calculated (solid line) $k^3\chi(k)$ functions (a) (k range: 3.45−14.45 $Å^{-1}$) and their Fourier transforms (b) for PcRu(n-BuNH$_2$)$_2$ (**2**) (seven-shell model; see Table 3 for fit parameters).

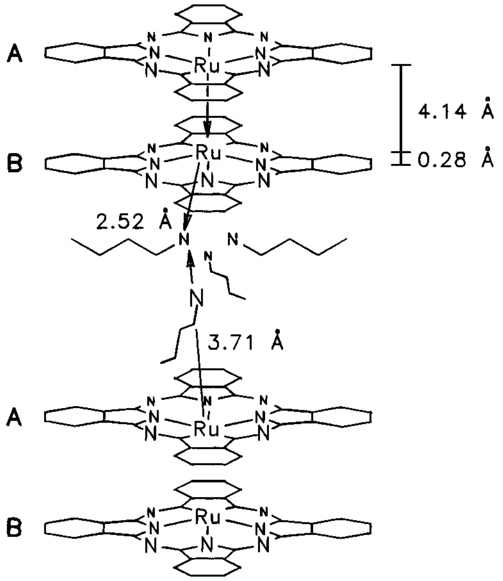

Figure 6. Structural model of PcRu(n-BuNH$_2$)$_2$ (**2**) including the assignment of the determined distances to the corresponding atoms (seven-shell model; see Table 3).

Ru−Ru and the out-of-plane distance we can calculate that the macrocycles are separated by at least 4.69 Å. That is an additional reason that the two nitrogen backscatterers can only be assigned to the n-butylamine ligand and not to the opposite-lying phthalocyanine molecule. Summarizing the results, we can deduce the complete structural model of PcRu(n-BuNH$_2$)$_2$ (**2**) that is shown in Figure 6.

Conclusion

From the EXAFS-determined data, it was possible to deduce detailed structural models for PcRu (**1**) (see Figure 2) and the bisubstituted PcRu(n-BuNH$_2$)$_2$ (**2**) (see Figure 6). The results for PcRu are in good agreement with those of Ercolani et al.,[3] except that we found that the next-neighboring phthalocyanine molecule is located at a shorter distance. The structure of PcRu(n-BuNH$_2$)$_2$ was a surprise for us, especially the fact that the n-butylamine ligands are located on one side of the macrocycle at such a long distance. We expected a normal 6-fold coordination of the ruthenium atom where the ligands are located on both sides of the phthalocyanine molecule, which follows from all theoretical[15] and experimental facts known so far. But the EXAFS data led to the model given in Figure 6. The observed structures are typical only for solid materials. We look forward now to investigating soluble PcRu's. Here we hope to determine significant changes in the local environment around the ruthenium center.

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