# X-ray Absorption Spectroscopy Studies of Ruthenoxane Phthalocyanine Derivative HO−[(Pc)RuO]$_n$−H

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Comprehensive EXAFS investigation carried out on ruthenoxane phthalocyanine and on its chemical precursors ruthenium phthalocyanine dimer and ruthenium bis-pyridine phthalocyanine are reported. The distances around the ruthenium atom were obtained by data analysis and confirm the structural models already proposed for the first two compounds and indicate two pyridines axially coordinated to the central metal for the adduct.

## Introduction

During work aimed at studying the behavior of metal phthalocyanines in the field of organic semiconductors, the authors have recently reported the synthesis and structural information of a polymeric derivative containing an oxygen atom bridging monomeric units of ruthenium phthalocyanine (**I**)[1] and of its precursor the ruthenium phthalocyanine dimer (**II**).[2a] The large angle X-ray scattering (LAXS) technique, suitable for investigation of short range order in amorphous samples, has been successfully employed for establishing a few important structural features for the studied systems.

For compound **I** the LAXS technique, supported by additional information (IR, EPR, ESCA, MS, and magnetic susceptibility data), has established that it consists of −(Pc)Ru$^{IV}$−O− fragments, linked together by linear Ru$^{IV}$−O−Ru$^{IV}$ bridges with the Ru atoms in the center of the planar Pc[2b] ring. The Pc rings are cofacially assembled with an inter-ring spacing of 3.69 Å, with staggering (35°) and eclipsing of the rings alternating along the stacking direction. This derivative appears to be the first example of a metalloxane stacked material showing, though undoped, significant electrical conduction properties ($\sigma_{RT} = 1 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$), with the central metal playing a decisive role for the charge transfer process. For compound **II** the presence of a direct short distance Ru−Ru bond (2.40 Å) in dimeric units has been pointed out and monodimensional stacking has been observed, six molecular units being superimposed along the stacking direction (parallel to the Ru−Ru bond). The conductivity value of this material, higher than those observed for monomeric and generally nonconducting metal phthalocyanines, could be explained if we consider the peculiar array of the dimeric units in (RuPc)$_2$ which allows some flow of electric charge through the Π system of the phthalocyanine rings as the average distance along the stacking direction is 3.36 Å. It is worth noting that although the RuPc has been the object of interesting studies[3] because of its properties, single-crystal structures have not yet been reported for any one of its derivatives if exclusion is made for RuPc(1MeIm)$_2$[4] and for the RuPc(DMSO)$_2$ that is reported to be isomorphous with FePc(DMSO)$_2$.[5] Because the bond lengths and electronic configuration in these systems are of primary interest, the authors have undertaken X-ray absorption spectroscopy (EXAFS) of the ruthenoxane derivative (**I**), (RuPc)$_2$ (**II**), and RuPc(Py)$_2$ (**III**) as EXAFS studies provide very accurate structural information for samples which do not possess long-range order. Preliminary results on the same samples and on a RuPc film have already been reported in a short communication.[6] In this paper the comprehensive results and all structural information for the metal site are compared with information previously obtained on the same systems and with related species.

## Experimental Section

All solvents and chemicals were used as pure reagent grade and freshly distilled if necessary. Elemental analyses were performed by Servizio di Microanalisi, Area della Ricerca, CNR; conventional X-ray powder diffraction patterns were recorded on a Seifert 3000 instrument with Cu Kα (50 KV, 30 mA) radiation; TGA thermogravimetric analyses were carried out on a DuPont 950 instrument under a stream of $N_2$ (0.5 dm$^3$, m$^{-1}$); UV−visible solution spectra were recorded on a Cary 5 spectrophotometer; $^1$H NMR spectra were obtained with a Bruker WP 200 instrument at NMR Servizio (Area della Ricerca).

**Ruthenoxane Derivative (I).** HO−[(Pc)RuO]$_n$−H was synthesized by suspending (RuPc)$_2$ in ClNP and heating in the presence of $O_2$ at 150 °C for 15 h, while stirring. After cooling and filtration the solid was fully characterized as previously described.[1]

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[2] (a) Capobianchi, A.; Paoletti, A. M.; Pennesi, G.; Caminiti, R.; Ercolani, C. *Inorg. Chem.* **1994**, *33*, 4635, and references therein. (b) Abbreviations used in the present paper: Pc = phthalocyaninato dianion, $C_{32}H_{16}N_8^{2-}$; DMSO = dimethyl sulfoxide; Py = pyridine; ClNP = α-chloronaphthalene; 1MeIm = 1-methylimidazole; 4MePy = 4-methylpyridine.

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**(Phthalocyaninato)ruthenium (II).** $(RuPc)_2$ was obtained by elimination of pyridine from $RuPc(Py)_2$ under vacuum as previously described.[2] The purity of the sample was checked by elemental analysis (calcd for $(C_{32}H_{16}N_8Ru)_2$, C, 62.64; N, 18.26; H, 2.63; found, C, 62.26; N, 18.23; H, 2.53). X-ray powder spectra were used to confirm the formation of the amorphous dimeric species.

**Bis(pyridine)(phthalocyaninato)ruthenium (III).** $RuPc(Py)_2$ was prepared, slightly modifying the procedure earlier reported,[7] by Soxhlet-extraction with pyridine of "crude RuPc." After cooling, purple crystals were obtained from the resulting blue solution and no further purification was needed. The complex was fully characterized by elemental analysis (calcd for $C_{42}H_{26}N_{10}Ru$: C, 65.35; H, 3.40; N, 18.1; found, C, 65.00; H, 3.25; N, 18.14), $^1H$ NMR [(200 $MH_z$, $CDCl_3$): $\delta$ 9.15 (8H, Pc), 7.93 (8H, Pc), 6.04 (1H, Py), 5.25 (2H, Py), 2.46 (2H, Py)], UV−vis spectra [(Py) = $\lambda_{max}$ 622 nm] and thermogravimetric analysis.

**EXAFS Experiment and Analysis.** We measured ruthenium K-edge EXAFS spectra at GILDA CRG beamline, ESRF, Grenoble (France), equipped with a Si(311) crystal in dynamic sagittal focusing mode monochromator, with a flux on the sample of about $10^9$ photons/second and with a focal image on the sample of about 1 $mm^2$.

EXAFS spectra in transmission have been recorded at ruthenium K-edge (21 126 eV), with a typical ring current of 125 mA for all the samples, at room temperature. All the samples have been finely ground and mixed with boron nitride and compressed in pellets in order to give an absorption coefficient ($\mu$) of about 3. The edge jump measured was in all cases of the order of 0.7. EXAFS spectra of 900 eV above the ruthenium K-edge were recorded while keeping k-spacing constant in order to collect between 500 and 600 data points, with an average acquisition time of 15 s.

EXAFS data analysis was performed using standard Daresbury programs to subtract the background from experimental spectra. The program EXCURVE 92 was used to fit the resulting EXAFS data and to obtain the structural parameters, employing a nonlinear least-squares curve fitting procedure. The Fast Curved Wave Theory, including multiple scattering processes (MS), was used to evaluate the contribution from the four highly symmetric pyrrolic rings about the metal ion up to the $\beta$ carbon atoms, using the minimum numbers of shells able to account for the contribution of multiple scattering from the atoms within the ruthenium plane. During all refinements the coordination numbers for all the shells considered and the geometric description of the pyrrolic rings was kept fixed and left unrefined using a maximum of five independent shells. The number of independent points $N = (dkdr/\pi) + 2$ exceeds 20 but a maximum of 10 parameters were used for the dimeric and the polymeric compounds.

The program EXCURVE 92 indeed offers the advantage of being able to describe the four symmetric rings around the absorbing ruthenium as a single rigid unit, with the relative distances and angles fixed and left unrefined. The first step in the analysis has been to refine parameters for the known crystal structure of the monomeric bis-adduct form $RuPc(1MeIm)_2$[4]. The $E_0$ value, $Ru-N_{(L)}$ (L = axial ligand) distance, and the relative disorder factor (total of 3 parameters) were refined using calculated phase-shift functions; and all other parameters were set at the known values from the crystallographic data. Once refined for compound **III**, the $E_0$ value was thoroughly employed. For the other two compounds only three shells were allowed to vary in distance and Debye−Waller factor for a total amount of six refined parameters: 1st = Ru-bonded nitrogen of pyrrolic ring; 2nd = Ru-bonded axial atom (either ruthenium for the dimer or oxygen in the polyner); 3rd = external nitrogens bridging the rings. The position of the four symmetric pyrrolic rings were refined using a single distance of the bonded nitrogen and its Debye−Waller factor. In addition to these parameters, the tilt of the phthalocyanine rings with respect to the molecular planes was allowed, introducing one more parameter for $\beta$ carbons and one for $\gamma$ carbons. One more shell was considered to account for the contribution from the outer molecular plane. In this way the maximum number of parameters was 10.

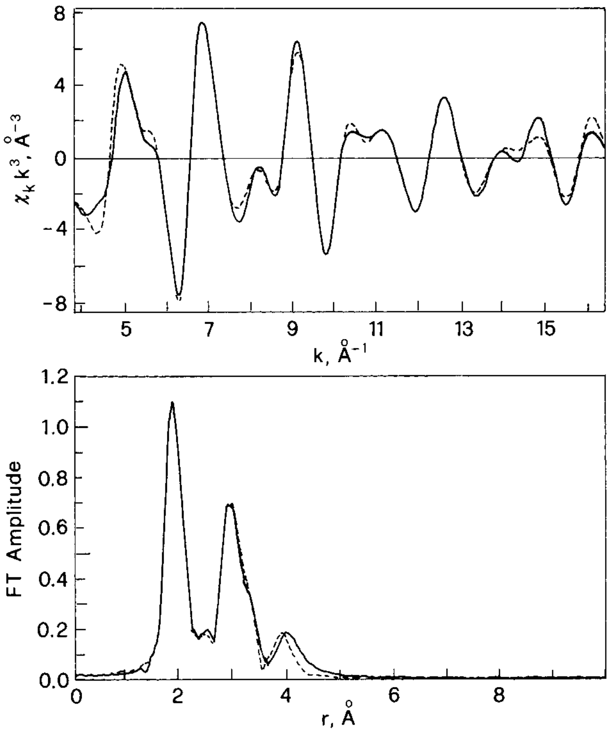

**Figure 1.** Above: observed (solid line) and calculated (dotted line) $k^3\chi(k)$ and (below) respective Fourier transforms for $RuPc(Py)_2$.

**Table 1.** EXAFS Determined Interatomic Distances ($r$) in $RuPc(Py)_2$; $\Delta E_0$=15.08 eV; Fit Index 0.5354[a]

| | $n$ | $r$ (Å) | $\sigma$ (Å) |
|---|---|---|---|
| Ru−N | 4 | 2.00 ± 0.01 | 0.039 |
| Ru−N(L) | 2 | 2.53 ± 0.01 | 0.072 |
| Ru−C | 4 | 3.01 ± 0.01 | 0.080 |
| Ru−C | 4 | 3.01 ± 0.01 | 0.016 |
| Ru−N | 4 | 3.33 ± 0.01 | 0.045 |
| Ru−C | 8 | 4.00 ± 0.01 | 0.063 |

[a] $n$ = coordination number; $\sigma$ = Debye−Waller type factor; (L) = pyridine ligand; all distances are referred to the same molecule.

## Results and Discussion

The results are presented starting from compound **III** because it was used as the reference for EXAFS analysis.

**Bis(pyridine)(phthalocyaninato)ruthenium(III).** In Figure 1 the experimental EXAFS spectrum of $RuPc(Py)_2$ is reported together with the calculated best fit and the respective Fourier transforms. In Table 1 the structural parameters used in the fit are listed.

To optimize the fitting, the mean positions of the atoms in the Pc ring were assumed to be approximately those found in $RuPc(1MeIm)_2$, and experimental parameters were fitted in the k space between 4 and 16 Å$^{-1}$. To minimize the number of parameters, we tested the minimum number of shells able to reproduce the experimental data. The MS contribution, due mainly to the $\beta$ carbons and the bridging nitrogens, is estimated to be on the order of 10%. It has also been noted that the coordinates of the $\beta$ atoms are not compatible with a perfectly planar arrangement of imidazole rings. This is evident both from the distances between the $\beta$ carbon atoms and the central ruthenium (3.012 Å), slightly shorter than expected if an average distance of 1.41 Å between nitrogen and carbon in the imidazole rings is assumed; as well as from the polar coordinates $\theta$ toward which the rings are tilted (4−6°). The environment around the ruthenium atom was satisfactorily described with four identical

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imidazole rings at 2.0 Å and four bridging nitrogens at 3.33 Å, and with two more nitrogens at a long distance of 2.53 Å. The Ru−N in-plane distances of 2.00 Å are apparently long for the ruthenium atom located in the center of the $N_4$ plane if we look at previous crystallographic data on similar planar systems, which report 1.97 Å as the longest found metal−nitrogen distance,[8,9] but an analogous value has been found for the hexacoordinate $RuPc(1MeIm)_2$ and more recently Homborg et al. reported average distances of 1.995−2.007 Å for several metal phthalocyanine derivatives,[10−13] deduced from single-crystal structures. In all these compounds the ligands are coordinated to the central metal in a trans arrangement indicating indeed that such distances are compatible with metals located in the center of the $N_4$ plane.

Furthermore, we have found X-ray powder spectra of microcrystalline $RuPc(Py)_2$ to be strictly isomorphous with the corresponding iron species, and we have verified the same correspondence for RuPc(4MePy) with respect to the structurally known $FePc(4MePy)_2$,[14] and $RuPc(DMSO)_2$ has been reported to be isostructural with $FePc(DMSO)_2$. This predictable analogy between the two metals, the calculated multiple scattering contribution, and the evidence of a very low disorder factor compatible only with two equal axial distances (see the $\sigma$ value in Table 1) support our assumption that in our case the ruthenium metal is in the center of the $N_4$ plane of the phthalocyanine ring and the two pyridines are trans coordinated to the metal. Our values, up to the fifth shells, are very close to those found by Bertagnolli and co-workers for the bis adduct buthyl amino derivative, but in that case different considerations led the authors to suggest an unusual structure where the two bases are coordinated on one side of the phthalocyanine molecule.[15]

**(Phthalocyaninato)ruthenium (II).** The EXAFS data and the bond distances are shown, respectively, in Figure 2 and Table 2. For this compound the phases, amplitudes, and parameters used for the bis adduct have been transferred unmodified to the dimeric form, leaving the single ring structure as described for the bis, and allowing geometric rearrangement of the rings with respect to the absorbing central atom of ruthenium; increasing the number of shells was considered (up to 9) for evaluating the Ru−Ru contribution from the second dimeric unit. Three main features characterize the experimental result: (i) the very clear contribution from the backscattering of a ruthenium atom at 2.39 Å; (ii) the contribution from two ring systems at different distances from the ruthenium; and (iii) the distance of 4.46 Å assigned between the absorber and the ruthenium of the next dimeric unit. The dimeric nature of this compound and the linear arrangement were already extensively demonstrated in a previous paper,[2] the bound distances found by EXAFS investigation confirm those obtained by LAXS technique and the model proposed consisting in dimeric units assembled in a stacked monodimensional array are also in perfect agreement with the relevant intra- and inter-dimeric distances shown in Table 2. Our results are in good agreement with the EXAFS study on the same compound reported by Bertagnolli et al.[15] with the exception of Ru−Ru interdimer distance found, by these authors, to be 3.52 Å, indeed shorter than expected considering the van der Waals interaction between the phthalocyanine rings in the suggested model, as it was also further discussed by Caminiti et al. in a recent contribution.[16]

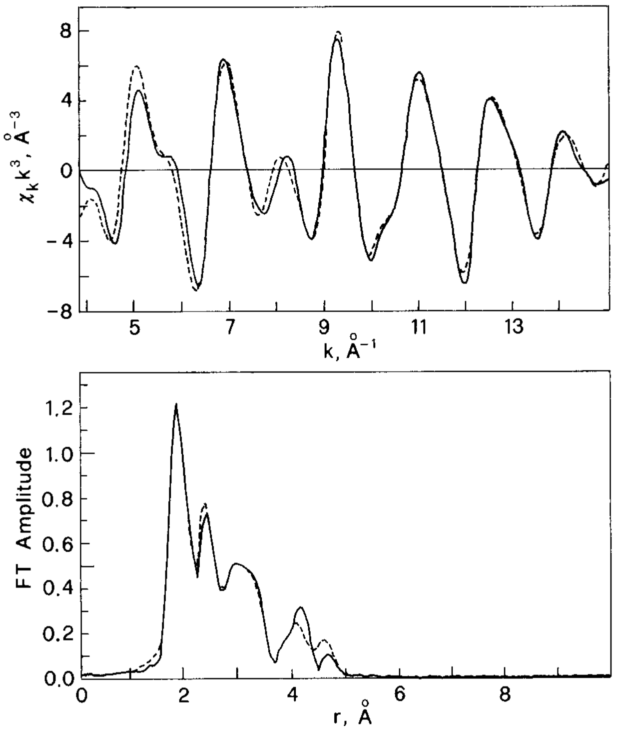

**Figure 2.** Above: observed (solid line) and calculated (dotted line) $k^3\chi(k)$ functions and (below) respective Fourier transforms for $(RuPc)_2$.

**Table 2.** EXAFS Determined Interatomic Distances ($r$) in $(RuPc)_2$; $\Delta E_0$ = 15.08 eV; Fit Index 0.863[a]

| | $n$ | $r$ (Å) | $\sigma$ (Å) |
|---|---|---|---|
| Ru−N(A) | 4 | 1.98 ± 0.01 | 0.035 |
| Ru−Ru(A′) | 1 | 2.39 ± 0.01 | 0.050 |
| Ru−C(A) | 4 | 3.00 ± 0.01 | 0.045 |
| Ru−C(A) | 4 | 3.00 ± 0.01 | 0.042 |
| Ru−N(A) | 4 | 3.19 ± 0.01 | 0.032 |
| Ru−N(A′) | 4 | 3.34 ± 0.01 | 0.016 |
| Ru−Ru(B) | 1 | 4.46 ± 0.01 | 0.047 |
| Ru−C(A′) | 4 | 4.01 ± 0.01 | 0.055 |
| Ru−C(A′) | 4 | 3.99 ± 0.01 | 0.061 |

[a] $n$ = coordination number; $\sigma$ = Debye−Waller type factor; A, A′ = Pc rings of the dimeric unit; B = Pc ring of the closest dimeric unit.

**Ruthenoxane Phthalocyanine (I).** For the third ruthenium phthalocyanine compound under investigation, already described as a polymeric oxo-bridged aggregate,[1] the experimental EXAFS was fitted keeping phase, amplitude, and ring description fixed and using the minimum number of parameters including $\beta$ and $\gamma$ carbon atoms from the in-plane rings. Two axial oxygens out of the plane and the contribution of the ruthenium atom of the closest phthalocyanine plane were also taken into account. In Figure 3 the experimental data and the fit are reported. The structural parameters are summarized in Table 3. The fitting optimization revealed a small amount of impurity (6%) showing a peak around 2.5 Å, likely attributable to the presence of unreacted ruthenium phthalocyanine dimer. The data indicate

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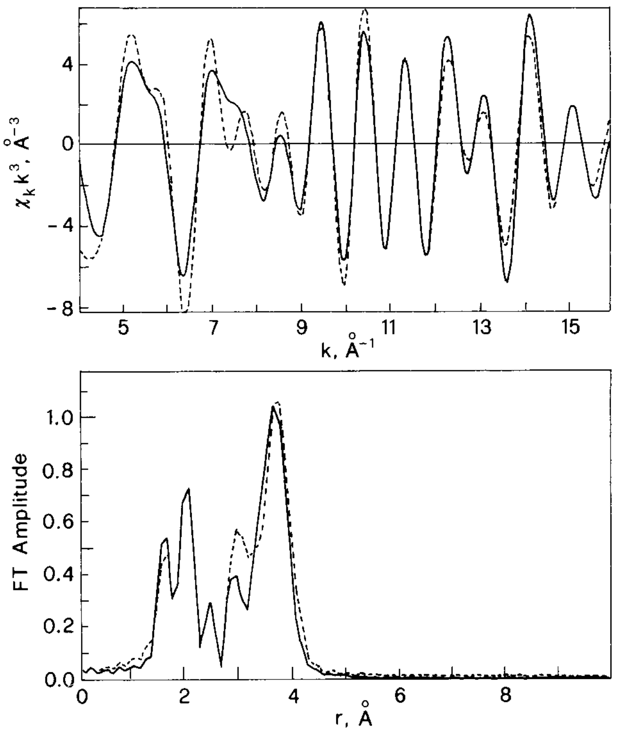

**Figure 3.** Above: observed (solid line) and calculated (dotted line) $k^3\chi(k)$ functions and (below) respective Fourier transforms for HO−[(Pc)RuO]$_n$−H.

**Table 3.** EXAFS Determined Interatomic Distances (*r*) in HO−[(Pc)RuO]$_n$−H; $\Delta E_0$ = 15.08 eV; Fit Index 2.93[a]

| | *n* | *r* (Å) | *σ*(Å) |
|---|---|---|---|
| Ru−N(1) | 4 | 1.99 ± 0.01 | 0.042 |
| Ru−C(1) | 4 | 2.98 ± 0.01 | 0.144 |
| Ru−C(1) | 4 | 2.97 ± 0.01 | 0.027 |
| Ru−C(1) | 4 | 3.89 ± 0.01 | 0.154 |
| Ru−C(1) | 4 | 3.95 ± 0.01 | 0.000 |
| Ru−O | 2 | 1.81 ± 0.01 | 0.045 |
| Ru−Ru(2) | 1 | 3.71 ± 0.01 | 0.032 |
| Ru−N(1) | 4 | 3.31 ± 0.01 | 0.039 |

[a] *n* = coordination number; *σ* = Debye−Waller type factor; (1), (2) = cofacial Pc rings linked by oxygen atom.

a very strong effect of forward scattering, due to a contribution at 1.80 Å of two oxygen atoms and 3.71 Å of two ruthenium backscatters, respectively; and the collinearity of the ruthenium−oxygen−ruthenium system is responsible for the very intense peak at 3.71 Å in the Fourier transform due to a very strong MS effect. Both distances are in good agreement with those found by LAXS investigation (1.84, 3.69 Å) and confirm the model in which two oxygens are axially linked to the ruthenium atom located in the center of the planar Pc ring, giving rise to a column stacked ruthenoxane aggregate. EXAFS preclude any consideration of the relative orientation of more distant rings; so we are not able to discuss the alternating staggering and eclipsing mode in the stack.

The in-plane Ru−N$_4$ distances of 1.99 Å show that the value of 1.92 Å, chosen as fixed parameter to fit the LAXS data, was underestimated. As a matter of fact the revised analysis of the LAXS data introducing the appropriate distance produced a slight fitting improvement as expected. The reported values of the Debye−Waller factors (*σ*), more evident for *γ* carbon atoms, indicate that some structural disorder is present in the sample, likely due to some steric hindrance or to the small amount of impurity present in the sample.

## Conclusion

The good quality fit of all the three examined compounds allowed us to determine bond distances with a high level of accuracy, permitting us to make precise deductions. The structural parameters obtained for the rutenoxane derivative formula (**I**) are in good agreement with those obtained by LAXS investigation detailing the structural model consisting of −(Pc)-Ru$^{IV}$−O− fragments linked together by linear Ru$^{IV}$−O−Ru$^{IV}$ bridges, the Pc rings being cofacially assembled with an inter-ring spacing of 3.71 Å. The data obtained for (RuPc)$_2$ confirm the dimeric structure of the complex and the stacking arrangement as previously reported. The analysis yielded bond lengths for the bis adduct RuPc(Py)$_2$ consistent with ruthenium located in the center of the N$_4$ plane and the two pyridine trans coordinated; although the Ru−N$_{Py}$ distance of 2.5 Å appears surprisingly long. Further investigation is underway to confirm these structural features.

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