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Ruthenium Phthalocyanine: Structure, Magnetism, Electrical Conductivity Properties, and Role in Dioxygen Activation and Oxygen Atom Transfer to 1-Octene

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Solid pure ruthenium phthalocyanine, obtained from its adduct [PcRu(DMSO)$_2$]·2DMSO, is an amorphous material, and its structure has been examined by the large-angle X-ray scattering (LAXS) technique. Experimental data are best fitted by assuming that ruthenium phthalocyanine is dimeric, i.e. (PcRu)$_2$, with a short intradimer Ru(II)−Ru(II) contact (2.40 Å), six dimeric units, on average, closely approaching one another and stacked in a monodimensional array. (PcRu)$_2$ is paramagnetic with a room-temperature magnetic moment (2.54 μ_B), which is strongly temperature dependent in the range 300−6 K. Interpretation of the magnetic behavior leads to an electronic energy level diagram which locates the highest energy electrons for the dimer in the orbital sequence $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$. The electrical conductivity value σ(RT), $1 \times 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, is also considered in the light of the structural features of the complex. (PcRu)$_2$, stable to air as a solid material, easily interacts with dioxygen when in contact with tetrahydrofuran. Dioxygen activation and oxygen atom transfer are observed for ruthenium phthalocyanine in the oxidation of 1-octene by O$_2$ in tetrahydrofuran, in the presence of (C$_6$H$_5$CN)$_2$PdCl$_2$ as the olefin activator, with selective formation of 2-octanone. Catalytic experiments were carried out at room temperature and at a p(O$_2$) of 50 atm. The optimized conditions for oxidation involve a Fe:Pd:olefin molar ratio of about 1:1.7:40.

Introduction

Reexamination of previous literature on the isolation and characterization of "ground PcRu" and of six-coordinate Ru(II) phthalocyanine derivatives of general formula PcRu(L,L′) (L or L′ = py and other N-bases, CO, DMSO, DMF, THF, etc.) only fairly recently led to reproducible pathways for the synthesis of pure PcRu,[1a] obtained, as previously indicated,[2] by the reaction of RuCl$_3$·xH$_2$O with *o*-cyanobenzamide and followed by the formation of the DMSO adduct, [PcRu(DMSO)$_2$]·2DMSO, and subsequent elimination of DMSO from the latter.[1a] Alternative, though similar, preparative methods, using the bis adducts PcRu(py)$_2$ and PcRu(quin)$_2$, were recently proposed.[1b] So far, in addition to the PcRu(L,L′) species,[1−3] linear-chain Ru(II) derivatives of formula [PcRu$^{\mathrm{II}}$L]$_n$ (L = bidentate N-base) are also known[1,4−6] whereas only the μ-nitrido species [PcRu]$_2$N[7a] and the anion [PcRuCl$_2$]$^-$ [7b] have been reported, which contain Ru in an oxidation state higher than II. Some specific contributions on ruthenium phthalocyanine have dealt with its electrochemical,[2] kinetic,[8,9] and photochemical behavior,[10] this latest implying the formation of the ligand-centered π-radical species [Pc(−1)Ru$^{\mathrm{II}}$(L,L′)]$^{\bullet+}$.

Although ruthenium phthalocyanine can certainly be a promising metal phthalocyanine compound in many respects, its structure, chemical physical behavior, and reactivity appear to be still largely unexplored. Despite extensive work carried out on the interaction of some first transition series metal phthalocyanines, particularly PcFe, with dioxygen,[11,12] no mention has so far been made in the literature of a similar reactive contact for PcRu, apart from a brief mention by Dolphin *et al.*,[2] with no details given.

In the present contribution, we show that ruthenium phthalocyanine is an amorphous material consisting of dimeric molecules stacked parallel to the axis of the intradimer Ru−Ru bond direction, with a short-range order (ca. 40 Å). Its solid state structure is examined in connection with its magnetic and electrical conductivity behavior. We also report the interaction of ruthenium phthalocyanine with dioxygen in tetrahydrofuran solution and the conversion of 1-octene into 2-octanone in the same medium using the Ru complex as catalyst.

Experimental Section

Pure ruthenium phthalocyanine was obtained from the adduct [PcRu(DMSO)$_2$]·2DMSO by thermal treatment (330 °C, 10^{-2} mmHg), as already described.[1a,7a] (C$_6$H$_5$CN)$_2$PdCl$_2$ was prepared as reported

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elsewhere[13] and its purity checked by elemental analysis. 1-Octene (Fluka) was purified by distillation and then passed through a column of Al_2O_3. THF, dried over sodium wire, was refluxed in the presence of sodium–benzophenone and distilled before use.

X-ray Data. The large-angle X-ray scattering (LAXS) technique is very useful for the investigation of the short-range order in amorphous systems[14] and was here applied to ruthenium phthalocyanine. This technique allows much of the information on amorphous or quasi-amorphous materials to be extracted from the static structure function $S(q)$, where q indicates the scattering parameter, i.e. $q = (4\pi/\lambda)(\sin\theta)$, or, equivalently, $q = (2/hc)E(\sin\theta)$, where 2θ = scattering angle, λ = radiation wavelength, E = radiation energy, and c and h have their usual meanings.

Since q depends on both E and θ, to execute a scanning in the reciprocal q space (obtaining the diffraction pattern), it is possible either (fixed E) to perform an angular scanning or (fixed θ) to do an energetic scanning, by means of a polychromatic X-ray beam and an energy-dispersive SSD (solid state detector) device.

In the present case, we used the second procedure, and diffraction data were collected with a noncommercial instrument,[15] comprising a white X-ray beam source and a germanium solid state detector connected with a multichannel analyzer. Specified here are the working conditions used. (a) Alimentation: high voltage = 55 kV, current = 35 mA, total power = 1.925 kW. (b) Energy interval utilized: 22.4–42.4 keV. (c) Measurement angles (θ): 21.0, 15.5, 10.5, 8.0, 5.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0°. (d) Scattering parameter interval (q): 0.4–15.4 $Å^{-1}$.

After the necessary corrections of the experimental data collected,[16] such as escape peak suppression, normalization to the incident radiation intensity, division by X-ray absorption and polarization coefficients, and elimination of inelastic scattering contributions, from the observed intensity $I(E,\theta)$, the static structure function, $S(q)$ (shown in Figure 1 as $q\ S(q)\ M(q)$; see below for $M(q)$), can be obtained. The Fourier transformation of the $S(q)$ function gives the radial distribution function (represented in Figure 2 as Diff(r) = $D(r) - 4\pi r^2\varrho_0$)

$$D(r) = 4\pi r^2\varrho_0 + 2r\pi^{-1}\int_0^{q_{\max}} q\,S(q)\,M(q)\sin(rq)\,\mathrm{d}q \quad (1)$$

where ϱ_0 is the average electronic density of the sample [$\varrho_0 = (\sum_i n_i f_i(0))^2 V^{-1}$], V is the stoichiometric unit volume chosen, and $M(q)$ is a modification function defined by

$$(f_{Ru}^{\,2}(0)/f_{Ru}^{\,2}(q))\exp(-0.01q^2) \quad (2)$$

A more detailed description of the apparatus and technique is given elsewhere.[15,17]

Catalytic Oxidation of 1-Octene. Catalytic experiments were performed in THF at room temperature and ambient O_2 pressure or at a $p(O_2)$ of 50 atm, by using a Berghof autoclave. (*Caution*: Explosions may be caused by long exposure of THF to a high dioxygen pressure when the temperature exceeds 20–25 °C.) Two identical samples, each one containing ruthenium phthalocyanine, $(C_6H_5CN)_2PdCl_2$ as cocatalyst, and 1-octene in THF (2 mL), together with a sample for the blank test (catalyst and/or cocatalyst absent), were used in all experiments. Different Ru:Pd:1-octene molar ratios were explored. At the end of each experiment, the samples were brought to ambient pressure; the solid, if any was present, depending on the particular experiment examined, was separated by filtration from the solution. THF was added to the filtrate up to the level of the initial volume (2 mL). The reaction mixture was quantitatively examined by GC analysis for the conversion of 1-octene into octanones. The GC apparatus, details of the column, and the procedure used for analysis were described elsewhere.[18]

Other Physical Measurements. IR spectra in the region 4000–200 cm^{-1} were taken on a Perkin-Elmer 783 spectrophotometer by using Nujol mulls between CsI plates or by using KBr pellets. UV–visible solution spectra were recorded on a Perkin-Elmer 330 spectrophotometer. Room-temperature magnetic susceptibility measurements were obtained by the Gouy method on a permanent magnet (7000 G, 0.7 T), by using a solution of $NiCl_2$ as calibrant. Variable-temperature magnetic susceptibility studies were performed by a commercial SQUID magnetometer (Quantum Design, B_{max} ca. 5 T); the nonlinear least-squares fitting procedure applied to experimental magnetic susceptibility data was developed by using the Marquardt–Levenberg algorithm, which implies an iterative method. X-Band EPR spectra were recorded on a Varian E-109 spectrometer; the field was calibrated with 2,2-diphenyl-1-picrylhydrazyl (DPPH). Conventional X-ray powder spectra were recorded on a Seifert 3000 instrument with Cu Kα (50 kV/30 mA) radiation. Elemental analyses were provided by the Servizio di Microanalisi at the Area della Ricerca (CNR). Thermogravimetric analyses were performed on a DuPont 950 instrument under a stream of N_2 (0.5 $dm^3\ min^{-1}$). Dc conductivity measurements were performed at room temperature by the four-probe technique using powder pellets of 1.0 or 0.8 cm (diameter), pressed at ca. 10^8 Pa.

Results and Discussion

Structure. PcRu shares similarities with several metal phthalocyanines, in that, for instance, (a) it can be sublimed unchanged (10^{-2} mmHg, 450 °C) and (b) it easily forms solid bis adducts with various donors (py, DMSO, etc.). PcRu, as obtained from analytically pure and diamagnetic [PcRu(DMSO)$_2$]·2DMSO, exists in a solid state form, which has been shown to definitely not be isomorphous (d_{exp}, I_{max}: 13.53, 662.0; 12.46, 512; 7.46, 109.5; 7.25, 114.5; 4.37, 83.0; 3.23, 275.5; 3.13, 118.0) with the β crystalline form known for several first transition series metal phthalocyanines.[19]

The X-ray powder spectra of samples of PcRu obtained from different preparations are all identical to one another in number, shape, and relative intensity of peaks observed. The appearance, however, is typical of amorphous materials with a short-range order. This feature prompted an attempt to interpret these spectra by the use of the large-angle X-ray scattering (LAXS) technique.[14–17] One of the samples, having the correct elemental analysis (C, H, N), was exposed to X-rays under the experimental conditions previously specified for this technique (see Experimental Section). The fitting of the experimental structure function was accomplished by using the Debye function

$$S(q)_{ab} = \sum f_a f_b(\sin(r_{ab}q))(r_{ab}q)^{-1}\exp(-(1/2)\sigma_{ab}^{\,2}q^2) \quad (3)$$

where σ_{ab} = rms variation of the distance r_{ab}. The theoretical peaks are calculated by a corresponding Fourier transformation of the theoretical intensities for the pair interactions (eq 3), using the same modification function, $M(q)$ (eq 2), and the same q_{max} value (see eq 1) as for the experimental data.

In order to direct the fitting to optimization, the mean positions of atoms in the Pc ring were assumed to be approximately those found in the PcRu(py)$_2$[20] and in [PcFe(mim)]$_2$O·PcFe(mim)$_2$·3Me$_2$CO.[12] The following predictable structural features were also taken into account.

(a) Occurrence of direct Ru–Ru bonds in dimeric units: This kind of molecular association has been found or assumed in

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Table 1. Final Values of the Adjusted Parameters (Rms σ_{ab}) for the Model Used

$0 < r \leqslant 1.7$ Å	$\sigma_1 = 0.065$
$1.7 < r \leqslant 3.45$ Å	$\sigma_2 = 0.09$
$3.45 < r \leqslant 4.20$ Å	$\sigma_3 = 0.15$
$4.2 < r \leqslant 6.20$ Å	$\sigma_4 = 0.28$
$6.20 < r \leqslant 16.0$ Å	$\sigma_5 = 0.52$
$16.0 < r \leqslant 22.0$ Å	$\sigma_6 = 0.72$
$r > 22.0$ Å	$\sigma_7 = 0.80$

$Ru_2(C_{22}H_{22}N_4)_2$,[21] $Ru_2(OEP)_2$, and $Ru_2(TPP)_2$[22] and in dimeric Ru(II) carboxylates[23] and similar complexes.[24,25]

(b) Nonrigidity of the phthalocyanine ring: Some flexibility of this macrocyclic ligand, which tends to be strictly planar because of the extended π-electron delocalization, has been normally observed whenever adjacent ligand units are forced to significantly approach one another under the attracting force of a central metal. Examples of appreciable distortion from planarity have been observed, for instance, in several sandwich type molecules of formula Pc_2M.[26] Dimeric Ru(II) porphyrinates also show a domed position of the ligands.[22]

(c) Relative position of adjacent phthalocyanine units: It has been observed that a staggered position of adjacent phthalocyanine units is largely preferred especially when the arrangement leads to interunit distances shorter than 3.4 Å. This is particularly evident in sandwich-type molecules,[26] in single-atom-bridged dimers,[27] and in a number of partially oxidized species.[28]

(d) Monodimensional stacking of dimeric units: Stacking by monodimensional superimposition of molecules easily takes place as determined by the square planar structure of the phthalocyanine molecular sheets.

The only independent parameters used for the fitting were the mean square deviations of the interatomic distances. However, to each distance falling within a preset range ($0 < r \leqslant 1.7$ Å etc.) was assigned the same value of mean square deviation, so that the number of adjusted parameters was much smaller than the number of pair distances existing in the proposed model (Figure 3). The final values of adjusted parameters (rms σ_{ab}) for the model used are given in Table 1.

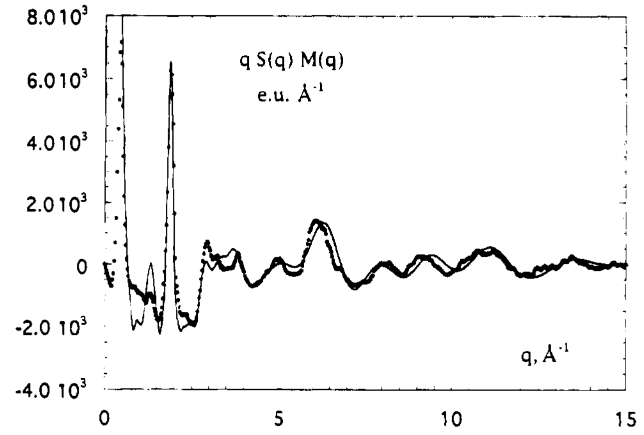

Figure 1. Observed (•••) and calculated (—) $q\ S(q)\ M(q)$ values vs $q = (4\pi/\lambda)(\sin\theta)$.

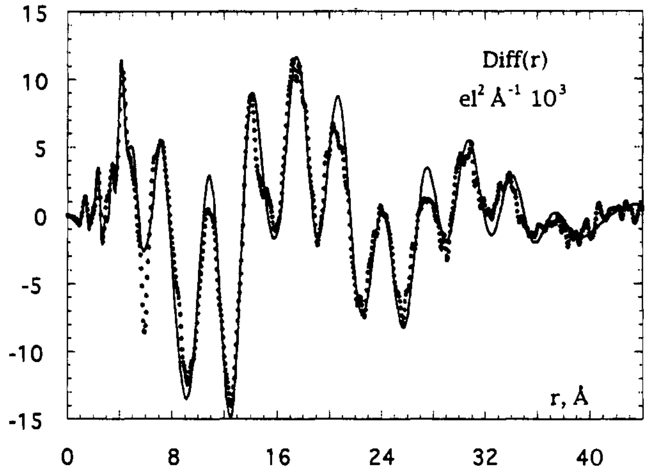

Figure 2. Experimental function $\mathrm{Diff}(r) = D(r) - 4\pi r^2\varrho_0$ (•••) and the theoretical calculated function (—), as illustrated in the text.

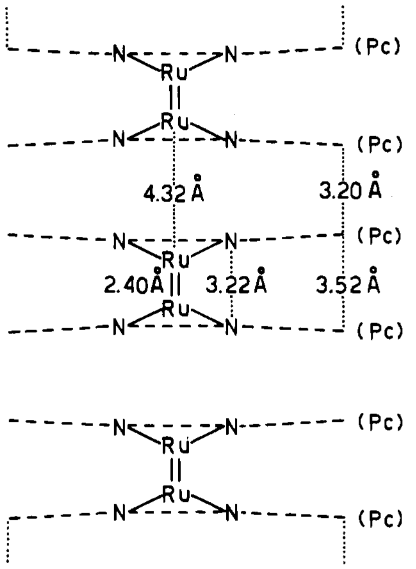

Figure 3. Stacking of $(PcRu)_2$ molecules parallel to the Ru–Ru axis.

The best fitting, shown in Figures 1 and 2, leads to the schematic structural representation of Figure 3. In detail, it establishes that (i) ruthenium phthalocyanine consists of dimeric molecules, i.e. $(PcRu)_2$, with short Ru–Ru bonds (2.40 Å), six molecular units, on average, being superimposed along the stacking direction (parallel to the Ru–Ru bonds; Figure 3), (ii) each ruthenium atom within the dimer is 0.41 Å out of the plane of the inner N_4 system of the respective macrocyclic ring, moving toward the other Ru atom, with Ru-N bond lengths of 1.97 Å, (iii) adjacent Ru atoms belonging to different dimers are 4.32 Å away from one another, (iv) the two phthalocyanine rings within the dimer are not perfectly planar and assume a domed conformation, each ring being slightly bent outward from

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Table 2. Structural and Magnetic Data for $(PcRu)_2$ and Similar Ru−Ru Dimers

complex	Ru−Ru (Å)	Ru−N (Å)	Ct−Ru (Å)	rotn (deg)	μ_{eff} (μ_B)	ref
$(PcRu)_2$	2.40(1)	1.97(1)	0.41(1)	45	2.54	this work
$Ru_2(OEP)_2$	2.41	2.05	0.30	23.8	2.8	22
$Ru_2(C_{22}H_{22}N_4)$	2.38				2.88	21
$Ru_2(O_2CR)_4$	2.26[a]				ca. 3.0[b]	23a
$Ru_2(hdpy)_2$[c]	2.24−2.26				ca. 2.3−2.8	24

[a] R = mandelate. [b] R = C_6H_5, CPh_3. [c] hdpy = hydroxypyridinate.

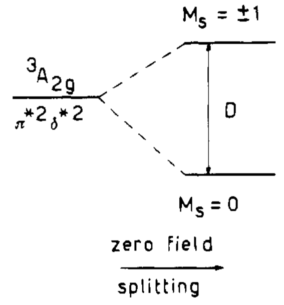

Figure 4. Schematic energy level diagram for $(PcRu)_2$.

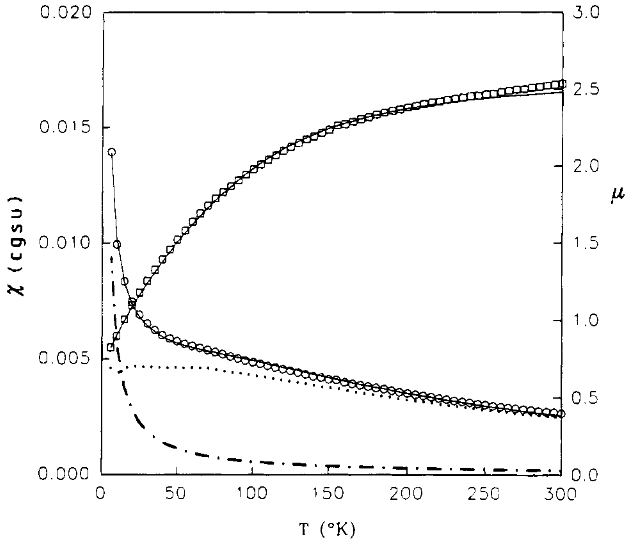

Figure 5. Temperature dependence of χ'_M vs T (K) (exp, ○○○; calcd, —; χ_0, •••; χ_{imp}, − • −) and μ_B vs T (exp, □□□; calcd, —). The correction for the diamagnetism of the Pc ligand is assumed to be 430 × 10^{-6} cgsu.

the inner N_4 plane (0.15 Å), and (v) within the dimer, the macrocycles assume a staggered position with a rotation angle of ca. 45°, staggering and eclipsing alternating along the stacking direction.

Other diruthenium complexes, known from single-crystal X-ray work, share several common features with $(PcRu)_2$ (Table 2). Of relevance are the Ru−Ru bond distances, found to be 2.38 Å in $Ru_2(C_{22}H_{22}N_4)_2$ (taken from ref 22), 2.41 Å in $Ru_2(OEP)_2$,[22] 2.25−2.30 Å in diruthenium tetracarboxylates,[23a] 2.24−2.26 Å in diruthenium 2-hydroxypyridinates,[24] and 2.42 Å in triazeno complexes, $Ru_2(RNNNR)_4$,[25] very close to the value obtained for $(PcRu)_2$. Among these cited species, $Ru_2(OEP)_2$,[22] due to the nature of the macrocyclic ring (N_4 inner system), is the one structurally resembling more closely $(PcRu)_2$ at the molecular level. As can be seen from Table 2, the metal atom in $Ru_2(OEP)_2$ is 0.30 Å from the center of the respective N_4 plane, with Ru-N bond distances of 2.05 Å, features not unreasonably different from those of $(PcRu)_2$, if account is taken of the more expanded core dimensions of the porphyrin macrocycle with respect to that of the Pc ring; the domed conformation of the two porphyrin rings in $Ru_2(OEP)_2$ is associated with a twisting angle of 23°.

To our knowledge, $(PcRu)_2$ appears to be the only well-identified dimeric species in the field of metal phthalocyanines.

Magnetic and Electrical Conductivity Properties. Detailed magnetic susceptibility studies have been carried out for the several ruthenium dimers mentioned above.[23−25] Except for the case of the diamagnetic triazeno complexes,[25] the interpretation of the paramagnetism observed indicates the presence of two unpaired electrons ($S = 1$ spin state). In terms of a molecular orbital approach, the interpretation of the temperature dependence of the magnetic susceptibility has led to the formulation of the external electron energy level sequence $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$, suggesting a clean Ru(II)−Ru(II) double bond. Under the effect of spin−orbit coupling, splitting occurs for the spin-triplet state $^3A_{2g}$, which is suggested to be below the degenerate singlet states $^1A_{1g}$, $^1B_{1g}$, and $^1B_{2g}$, allowing an orbital singlet to lie lowest ($M_s = 0$) (see Figure 4). The separation (D) between M_s and the higher energy components $M_s = \pm1$ is comparable to kT, which determines the quenching of the magnetic moment with the lowering of the temperature. $(PcRu)_2$ shows a room-temperature magnetic moment of 2.54 μ_B (Table 2). This paramagnetism cannot be assigned, either entirely or even partially, to the occurrence of ligand-centered π-radical species, since $(PcRu)_2$, as a solid, is EPR silent, if exception is made of a low-intensity signal, evidenced at $g = 2$ at high gain values, already noticed,[7a] and clearly attributable to the presence of small amounts of paramagnetic impurities. Being metal-centered, the observed paramagnetism, while clearly exceeding the value expected for one unpaired electron, rather approaches that expected for two unpaired electrons. A considerable quenching of the magnetic moment is observed when the temperature is lowered to 6 K (0.82 μ_B). The experimental data for χ'_M vs T are plotted in Figure 5. The observed magnetic behavior is similar to that shown by the dimeric analogues already referred to above.[23,24] The steep rise of χ'_M at low temperature suggests the presence of a paramagnetic contaminant, assumed to obey the Curie law. No certain indication of the nature of the contaminant can be given. In keeping with the perfect elemental analyses of the sample of $(PcRu)_2$ used, we suggest it to be the unknown monomeric PcRu, containing Ru(II) (d^6) reasonably having a spin state S = 1. Within this assumption, we have attempted a fit of the observed χ'_M values with those calculated on the basis of the combined use[23,24] of the equation

$$\chi'_M = (1 - \alpha)\chi_0 + \alpha\chi_{imp}$$

[where α represents the mole fraction of the contaminant and χ_0 and χ_{imp} are the molar susceptibilities of $(PcRu)_2$ and of the impurity, respectively] and of the expression for a clean paramagnet, valid if the singlet state is assumed to lie lowest

$$\chi_M = \frac{2Ng_{eff}^2\mu_B^2}{3k_BT}\left(\frac{e^{-x} + (2/x)(1 - e^{-x})}{1 + 2e^{-x}}\right)$$

where $x = D/k_BT$, g_{eff} is the effective gyromagnetic ratio, k_B is the Boltzmann constant, μ_B is the Bohr magneton, N is Avogadro's number, and T is the temperature (K).

The nonlinear least-squares fit of the experimental data is shown in Figure 5. It affords the values $\alpha = 0.0562(5)$, $g = 1.81(1)$, and $D = 235$ cm^{-1}. The presence of 5.6% monomer impurity seems reasonable. After correction of χ'_M for the impurity, χ_0 is obtained, which is temperature independent at the lowest temperatures, as observed for similar examples.[23,24] The g and D values appear to be normal when compared to those observed for the other Ru dimers.[23,24] The obtained fitting of experimental χ'_M with the calculated values definitely indicates that the ground state in $(PcRu)_2$ is nonmagnetic. The similarity in magnetic behavior between $(PcRu)_2$ and the other studied Ru dimers[24,25] suggests the electronic structure $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ and the presence of a clean double bond in $(PcRu)_2$, in good agreement with the Ru–Ru bond distance observed. Lack of structural and magnetic information on monoelectronically oxidized $(PcRu)_2^+$ species, presently unknown, does not allow any type of correlation between Ru–Ru bond length and electronic structure, as it was indeed possible for the mentioned carboxylates.[23,24] The Ru–Ru bond length observed for $(PcRu)_2$, i.e. 2.40 Å, compares well with the values found for $Ru_2(C_{22}H_{22}N_4)_2$ and $Ru_2(OEP)_2$. These bond distances appear to be longer than those observed for the Ru carboxylates[23a] and Ru hydroxypyridinates,[24] this being due, at least partially, to the steric and electronic repulsion between the macrocyclic rings of the dimer, particularly in the case of the Pc and OEP ligands. The observed fitting for $(PcRu)_2$ also suggests that dimer contacts do not significantly affect the magnetic behavior. Evidently, encapsulation of the metal couples within the dimer does not favor intermolecular magnetic superexchange.

For $(PcRu)_2$ an electrical conductivity σ(RT) value of 1×10^{-5} Ω^{-1} cm^{-1} has been measured, which confirms previous findings.[29] This conductivity value is significantly higher than those observed for monomeric and generally nonconducting metal phthalocyanines ($<10^{-9}$–10^{-10} Ω^{-1} cm^{-1}). The observed σ(RT) value is in the range of values of semiconducting systems (10^{-6}–10^{-1} Ω^{-1} cm^{-1}). An explanation can be found in the peculiar ordering of the dimeric units in $(PcRu)_2$, which allows, owing to the observed close contacts of adjacent molecular units, some flow of electric charge through the π system of the phthalocyanine rings (average distance along the stacking direction 3.36 Å).

Interaction with Dioxygen. Dissolution of $(PcRu)_2$ in THF in the presence of dioxygen or in air is accompanied by a rapid color change of the solution from bluish-green to blue. Correspondingly, the UV–visible absorption spectrum of the solution changes, as shown in Figure 6. Initially, the spectrum shows an intense maximum at ca. 290 nm and lower intensity visible absorptions at 420 and 695 nm, with an intermediate more intense absorption at 598 nm (spectrum 1). The spectral change, which normally goes to completion within ca. 1 h and determines the formation of isosbestic points at 295, 400, 530, and 675 nm, causes (a) shifts of the maxima at 290 and 598 nm to 314 and 622 nm, respectively, (b) disappearance of the 420 and 695 nm absorptions, and (c) appearance of a new lower intensity maximum at 354 nm (spectrum 5). The observed presence of isosbestic points clearly excludes the formation of spectrally detectable intermediates in going from spectrum 1 to spectrum 5. This latter cannot be reversed to spectrum 1 simply by flushing prepurified N_2 into the solution. In a previous report, no mention was made of the above spectral change and the spectrum of a solution of ruthenium phthalocyanine in THF was given with a maximum intensity absorption at 627 nm.[3] This spectrum is very similar to that observed by us as the final spectrum (spectrum 5), although the position of the most intense absorption differs slightly.

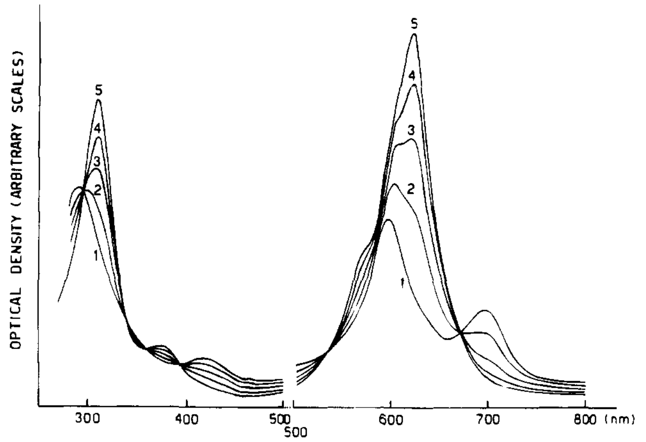

Figure 6. UV–visible spectral variations (curves 1–5) for solutions of $(PcRu)_2$ in THF in the presence of air or of pure dioxygen.

The above spectral changes are always observed, and normally achieve completion roughly within the same time, provided that the solution is equilibrated with an atmosphere of gaseous O_2 (or air) and no matter what the type of THF used, i.e. (a) taken directly from the bottle, (b) preliminarily distilled, (c) dried by refluxing it in the presence of Na–benzophenone, followed by distillation in an inert atmosphere, and (d) prepurified of peroxides by passing it through a column of alumina. Instead, extremely small changes in the spectrum are observed if ruthenium phthalocyanine is dissolved in freshly distilled and peroxide-free THF in the "rigorous" absence of dioxygen. Definitely, then, the above spectral behavior is assigned to the interaction of ruthenium phthalocyanine with O_2. In a number of experiments, it was observed that even traces of oxygen in the medium can result in instability of the spectrum with qualitatively identical, although kinetically definitely slower, changes (spectra 1–5). The most effective method for the registration of the initial spectrum consists of rapid dissolution of a sample of ruthenium phthalocyanine in THF, with consequent immediate recording of the spectrum. Difficulties with these spectral observations have been encountered in obtaining kinetically reproducible results, even when parallel experiments were carried out with apparently identical procedures, probably because of problems originating from the particular nature of the solvent and its intriguing interaction with molecular oxygen. It seems reasonable to assume that dissolution of $(PcRu)_2$ in THF immediately transforms the dimer into the monomeric bis adduct $PcRu(THF)_2$. This is suggested by the facts that (a) in solutions of poorly coordinating or noncoordinating solvents, such as CH_2Cl_2 and $CHCl_3$, where $(PcRu)_2$ presumably maintains its dimeric structure, the complex shows its main visible absorption considerably shifted to higher wavelengths, i.e. at 641 and 640 nm, respectively, and (b) $(PcRu)_2$ is known to easily give bis adducts, i.e. $PcRu(L)_2$, with L = pyridine and even DMSO. Furthermore, $(PRu)_2$ dimers (P = porphyrinato anions) have been proved to give the adducts $PRu(THF)_2$ by dissolution in THF.[30] The kinetic and mechanistic aspects of the interaction of ruthenium phthalocyanine

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Table 3. Catalytic Oxidation of 1-Octene in THF in the Presence of Ruthenium Phthalocyanine as Catalyst and the Pd Complex as Cocatalyst[a]

expt	amt of PcRu (mg (mmol)[c])	amt of Pd (mg (mmol))	amt of oct-1-ene (μL (mmol))	*t* (h)	TN[b] (mmol of 2-octanone/mmol of PcRu[c])
1	10 (0.016)	10 (0.0275)	100 (0.63)	1	1.0–1.2
2	10 (0.016)	10 (0.0275)	100 (0.63)	3	2.6–4.0
3	10 (0.016)	10 (0.0275)	100 (0.63)	5	4.5–6.0
4	10 (0.016)	10 (0.0275)	100 (0.63)	8	6.7
5	10 (0.016)	10 (0.0275)	100 (0.63)	10	6.5–8.0
6	10 (0.016)	10 (0.0275)	100 (0.63)	22	9.0–12.0
7	10 (0.016)	5 (0.014)	100 (0.63)	22	1.5–2.0
8	10 (0.016)	20 (0.055)	100 (0.63)	22	9.0–11.0
9	filtered satd solns	10 (0.0275)	100 (0.63)	22	10.0–12.0

[a] In experiments 1–8 only ca. 8–8.5 mg of ruthenium phthalocyanine was dissolved and 1.5–2.0 mg was present as a solid residue. [b] TN (turnover number); average values of several experiments. [c] Millimoles of ruthenium phthalocyanine calculated on the basis of the monomeric form.

with dioxygen in THF, as well as isolation and characterization of solid oxygen-containing ruthenium phthalocyanine derivatives, are presently the object of further investigation.

Oxidative Catalysis by O_2. The metal-assisted catalytic and selective oxidation of terminal olefins to the corresponding methyl ketones or epoxides by dioxygen or other oxidizing agents is a process of practical interest. Attempts to use PcFe or other metal phthalocyanines for such types of metal-assisted oxidations have been less[31] and more recently reported.[32–35] Effective interaction of ruthenium phthalocyanine with dioxygen has been evidenced here for the first time. In an attempt to demostrate that this process can determine dioxygen activation followed by oxygen atom transfer to an external substrate, we have investigated the possibility of oxidation of 1-octene to octanones in THF by using dioxygen as the oxidant, ruthenium phthalocyanine as the catalyst, and $(C_6H_5CN)_2PdCl_2$ as the cocatalyst, i.e. as the olefin activator.[36]

Experiments were carried out at room temperature (20–25 °C) and ambient O_2 pressure or at $p(O_2) = 50$ atm. Details of the procedures are given in the Experimental Section. The use of ambient dioxygen pressure did not lead to significant conversion of 1-octene. Table 3 summarizes the experiments carried out in THF at $p(O_2) = 50$ atm.

Experiments 1–6 were carried out using 10 mg of ruthenium phthalocyanine (0.016 mmol), most of which dissolved (8 mg) in a solution (THF, 2 mL) of 10 mg (0.0275 mmol) of the Pd complex and 100 mg (0.63 mmol) of 1-octene (ratio Ru:Pd:1-octene = 1:1.7:39.4). These experiments show that the oxidation process is in general catalytic, with the maximum value of the turnover number at times of ca. 22 h. In all cases, the reaction is very selective; i.e., 2-octanone is almost exclusively formed (98–100%), with traces of 3-octanone (0–2%) and practically no 4-octanone present. Experiments 7 and 8 show that 10 mg of the Pd cocatalyst is the minimum appropriate amount to be used. Increasing this amount (experiment 8) does not result in a higher yield of 2-octanone.

A number of experiments were carried out by using saturated solutions (ca. 8 mg in 2 mL of THF) (experiment 9), with results comparable to those carried out in the presence of a slight excess of ruthenium phthalocyanine. These results clearly demonstrate that the catalytic process develops in solution, i.e. in a homogeneous phase. A few experiments carried out by using 1-decene in place of 1-octene gave similar results. Experiments were also performed by using $[PcRu(DMSO)_2]\cdot 2DMSO$ and $PcRu(py)_2$ as catalysts with no conversion of the olefin. This implies that ligation of relatively strong donors at the axial coordination sites inhibits dioxygen activation and oxygen atom transfer.

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