

Dimeric Osmium Phthalocyanine Organized in Discrete Columnar Stacked Assemblies: Structure, Magnetism, and Electrical Conductivity Properties

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Solid pure osmium phthalocyanine, as obtained from its adduct [PcOs(py)]₂, is an air-stable solid amorphous material. Its structure has been examined by the wide-angle X-ray scattering (WAXS) technique. Experimental data are best fitted by assuming the molecule to consist of a dimeric unit, (PcOs)₂, held together by a direct metal–metal linkage. The short Os–Os distance (2.38(1) Å) is consistent with the presence of a double bond between the two Os(II) atoms. Each Pc skeleton has a domed conformation with displacement of the respective Os atom from the plane of the four coordinating nitrogen atoms (0.40 Å) toward the other Os atom. The solid-state structure consists of disordered couples of parallel chains of (PcOs)₂. On average, six dimeric units are aligned along the stacking direction within each chain. The relative orientation of the two intradimer Pc units is 30°, eclipsing occurring for the interdimer adjacent Pc units along the chain. Magnetic susceptibility measurements in the temperature range 5–300 K indicate a strong spin–spin coupling for the two metal centers in the dimer and suggest an electronic energy level sequence $\sigma^2\pi^4\delta^2\delta^*2\pi^*2$ and a nonmagnetic ground state for the complex. Room-temperature electrical conductivity measurements show a σ_{RT} value of $1 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$.

Introduction

It has previously been established by the WAXS (wide-angle X-ray scattering) technique that ruthenium(II) phthalocyanine, a solid powdered amorphous material, consists of columnar arranged dimeric units, [(PcRu)₂]_n (average $n = 6$), with a short Ru–Ru bond distance within each dimer (2.40 Å) and longer interdimer Ru···Ru contacts (4.32 Å).^{1a} This dimeric species enters the short series of reported Ru–Ru dimers involving the use of macrocyclic molecules, i.e., porphyrins,² or other kind of ligands.³

Isolation of single crystals suitable for X-ray work is rare in the case of (ML)₂ complexes, L being a phthalocyanine or porphyrin ligand, and the structure has been solved only for the porphyrin derivatives [(OEP)Ru]₂⁴ and [(TPP)Mo]₂.⁵ Very recently, two new phthalocyanine dimers, i.e., (PcIr)₂ and (PcRh)₂, have been reported, but elucidation of the structure by X-rays has only been achieved on their bis(pyridine) adducts, [PcM(py)]₂.⁶ So far, then, (PcRu)₂ appears to be the only (PcM)₂ species for which detailed structural information has been reported.^{1b} It is shown here that osmium phthalocyanine

also consists of dimeric units (PcOs)₂. The use of the WAXS technique, combined with a detailed magnetic investigation and electrical conductivity measurements, has allowed us to throw some light on the structural and electronic properties of this new homobimetallic dimer.

Experimental Section

A previously reported procedure⁷ was used for the synthesis of the bis(pyridine) adduct PcOs(py)₂. Anal. Calcd for C₄₂H₂₆N₁₀Os: C, 58.59; H, 3.04; N, 16.26. Found: C, 58.27; H, 2.98; N, 16.00. Elimination of pyridine was obtained by heating PcOs(py)₂ at 320–330 °C under vacuum (10⁻²–10⁻³ mmHg) for 1 h to give pure osmium phthalocyanine. Anal. Calcd for the formula C₃₂H₁₆N₈Os: C, 54.69; H, 2.30; N, 15.95. Found: C, 55.00; H, 2.19; N, 15.99. Found after 4 months: C, 54.55; H, 2.25; N, 15.85.

X-ray Data. Information about the noncommercial X-ray energy scanning diffractometer constructed at the Department of Chemistry, University of Roma "La Sapienza" Powder Diffraction Laboratory, was given elsewhere.⁸ The procedure used for the collection of diffraction data was previously reported for (PcRu)₂^{1a} and has been applied similarly for the present case under the following experimental conditions. (a) Alimentation: high voltage, 45 kV; current, 35 mA; total power = 1.575 kW. (b) Energy interval utilized: 16.5–41.0 keV. (c) Measurement angles (θ): 26/21/15.5/10.5/8/5/3.5/3/2/1.5/1°. (d) Scattering parameter interval (q): 0.3–15.3 Å⁻¹.

The WL lines in the energy range 8–11 keV and the fluorescent X-ray from Os fell outside of the energy range explored. The transmission geometry has been employed, since it allows an easier

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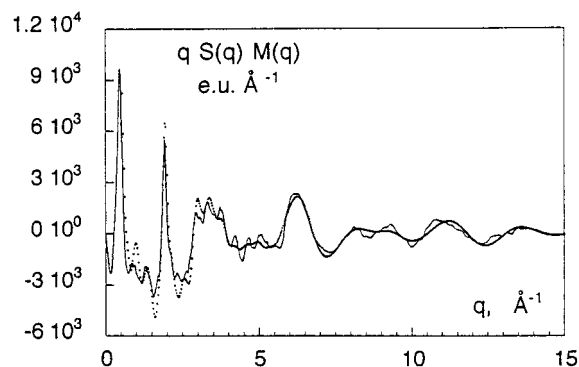


Figure 1. Observed (—) and calculated (···) $qS(q)M(q)$ values vs q .

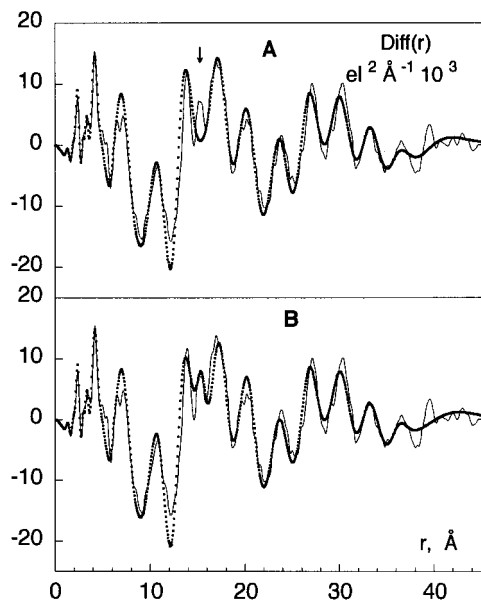


Figure 2. Experimental function $\text{Diff}(r) = D(r) - 4\pi r^2 \rho_0$ (—) and the theoretical calculated function (···), as illustrated in the text.

correction for the sample absorption.^{8c} After the necessary corrections of the experimental data collected, use has been made of the static structure function $S(q)$, where q indicates the scattering parameter, i.e., $q = (2/hc)E(\sin \theta)$, where $2\theta =$ scattering angle, $\lambda =$ radiation wavelength, $E =$ radiation energy, and c and h have their usual meanings. The Fourier transformation of the $S(q)$ function (shown in Figure 1 as $qS(q)M(q)$) gives the radial distribution function (shown as $\text{Diff}(r) = D(r) - 4\pi r^2 \rho_0$ in Figure 2) in which

$$D(r) = 4\pi r^2 \rho_0 + 2r\pi^{-1} \int_0^{q_{\max}} qS(q)M(q) \sin(rq) dq \quad (1)$$

where ρ_0 is the average electron density of the sample [$\rho_0 = (\sum n_i f_i(0))^2 V^{-1}$], V is the stoichiometric unit volume chosen, and $M(q)$ is a modification function defined by

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

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. 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 Marquardt–Levenberg's algorithm, which implies an iterative method. Room-temperature X-band EPR spectra were recorded on a Varian E-109 spectrometer. Conventional X-ray powder spectra were recorded on a Seifert 3000 instrument with a Cu $K\alpha$ (50 kV/30 mA) radiation. Elemental analyses were provided by the Servizio di Microanalisi, Dipartimento di Chimica at "La Sapienza".

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

r range (Å)	σ
0 < r ≤ 1.7	σ_1 0.06
1.7 < r ≤ 3.45	σ_2 0.09
3.45 < r ≤ 6.4	σ_3 0.25
6.4 < r ≤ 15.6	σ_4 0.46
r > 15.6	σ_5 0.73

Thermogravimetric analyses were performed on a DuPont 950 instrument under a stream of N_2 (0.5 $\text{dm}^3 \text{min}^{-1}$). Dc conductivity measurements were performed at room temperature by the four-probe technique using powder pellets, 1.0 or 0.8 cm (diameter), pressed at ca. 10^8 Pa.

Results and Discussion

Structure. Osmium phthalocyanine is a solid stable-to-air material. Its IR spectrum in the range 4000–200 cm^{-1} is practically superimposable on that of $(\text{PcRu})_2$. The complex is thermally stable up to temperatures of 350–400 °C in an inert atmosphere or under vacuum as indicated by its IR spectrum and elemental analyses performed before and after the thermal treatment. Its X-ray powder spectrum is as expected for an amorphous material; thus, the possibility was offered for the examination of pure samples of osmium phthalocyanine by the WAXS technique. To develop the fitting of the experimental structure function $qS(q)M(q)$ (Figure 1), use was made of the Debye function

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

where σ_{ab} = rms variation of the distance r_{ab} . The theoretical peaks were 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.

Table 1 lists the final values of adjusted parameters (rms σ_{ab}) for the model used (see below Figure 4) for the distance ranges examined. The best fitting, shown in Figures 1 and 2, definitely establishes the dimeric structure of osmium phthalocyanine. Figure 2A illustrates the type of fitting obtained by assuming that, on average, isolated chains of six columnarly stacked dimers are present in the solid state of the osmium complex. Clearly, in such a case, the experimental peak present at 15.4 Å (arrow) is absent in the calculated curve. A significant improvement of the fitting is obtained if the hypothesis is made of the presence of couples of chains arranged parallel to one another (Figure 2B). The peak at 15.4 Å in Figure 2B represents the distance between corresponding atoms belonging to the molecular units at the same level in the two adjacent chains (for more elucidation see the figures and further discussion below).

Schematic representations of the detailed structural features of the Os complex are given in Figures 3 and 4. Figure 3 shows an intermediate side-top view of how the two chains of six dimers are relatively positioned in the solid material. The arrangement is such that corresponding Pc units in the two chains, for instance Pc units 1 and 1', have coincident positions along the growing direction of each chain, although they are relatively rotated (30°) in order to minimize interchain electronic repulsions. Figure 3 also shows that, within a single chain, the intradimer Pc units are twisted by 30° (see for instance Pc units 1 and 2; 45° in the Ru analogue^{1a}), eclipsing occurring between interdimer adjacent units along the chain. The observed staggering sequence, of the type 1–2, 3–4, 5–6, etc., is the

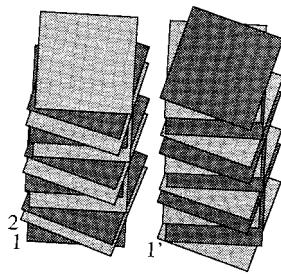


Figure 3. Intermediate side-top view of the arrangement of two adjacent chains of dimers.

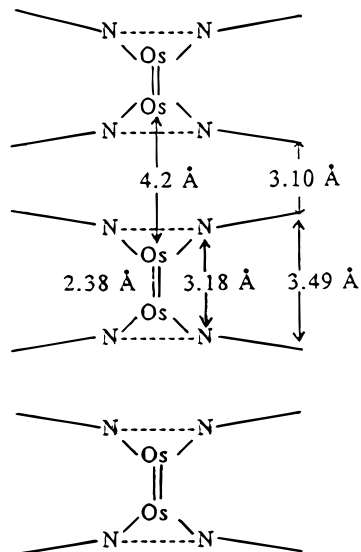


Figure 4. Schematic side view of the stacking of dimers of $(\text{PcOs})_2$ along a single chain.

same in the present Os species and in its Ru analogue,^{1a} while the eclipsing sequence is different, i.e., 2–3, 4–5, 6–7, etc., for the Os complex and of the types 1–3–5–7–9–11 and 2–4–6–8–10–12 for the Ru species.

A more detailed side representation of the structure for a single chain of the Os complex is given in Figure 4. The structure essentially resembles that found for $(\text{PcRu})_2$. The intradimer Os–Os bond distance is only a little shorter (2.38 Å) than that found for the ruthenium dimer (2.40 Å). Noticeably, (i) each Os atom within the dimer is 0.4 Å out of the plane of the inner N_4 system of the respective Pc unit, moved toward the other Os atom, with Os–N bond lengths of 1.96 (1) Å, (ii) adjacent Os atoms belonging to different dimers are 4.2 Å away from one another, a distance a little shorter than the corresponding distance in the Ru analogue (4.32 Å), and (iii) the two Pc rings within the dimer have a domed conformation, each ring being slightly bent outward from the inner N_4 plane (0.15 Å) in a manner very similar to that observed for $(\text{PcRu})_2$.

Magnetic and Electrical Conductivity Properties. The magnetic susceptibility of $(\text{PcOs})_2$ has been measured in the temperature range 5–300 K. The molar susceptibilities χ_M were calculated from the measured χ_g . The diamagnetic corrections applied were 430×10^{-6} and 44×10^{-6} cgsu for the Pc ligand^{1a} and the Os atom,⁹ respectively. The observed room-temperature magnetic moment calculated from the formula $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$ for the dimer is $2.07 \mu_B$. It is excluded that the observed paramagnetism be assigned to a ligand-centered

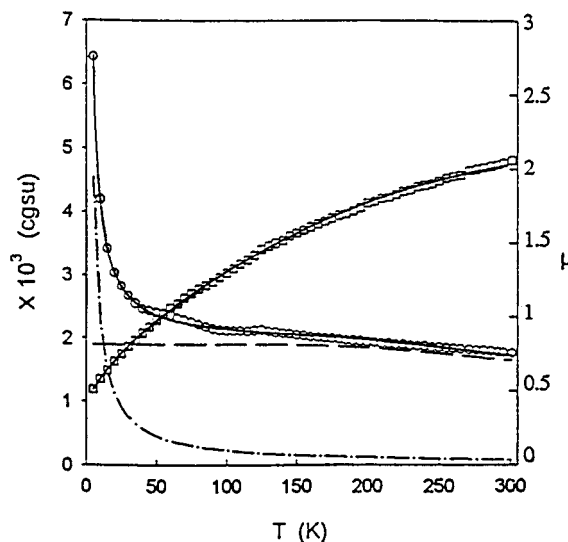


Figure 5. Temperature dependence of χ'_M vs T (K) (exptl, O; calcd, —; χ_0 , - -; χ_{imp} , - · -) and μ vs T (exptl, square; calcd, —).

π -radical species, since the complex is EPR silent, exception made for the presence of a low-intensity signal at $g \cong 2$ at high gain values due to the presence of subtle amounts of paramagnetic impurities, quite common for phthalocyanine materials. The measured μ_{eff} value is considerably below that observed for the corresponding Ru dimer ($2.58 \mu_B$) and even more far away from the spin-only value ($2.83 \mu_B$) calculated by assuming a direct contact between two Os(II) (d^6) centers and the semioccupation of the two π^* MO orbitals in the energy level sequence proposed for this kind of homobimetallic systems.³ In terms of this MO approach, splitting occurs for the $^3A_{2g}$ ground state under the effect of spin–orbit coupling allowing an orbital singlet to lie lowest ($M_S = 0$). The separation energy (D) between $M_S = 0$ and the higher energy components $M_S = \pm 1$ should be of the order of magnitude of kT ($\sim 200 \text{ cm}^{-1}$), as has been effectively observed for the ruthenium dimers so far investigated.^{2,3} On this basis, a quenching of the magnetic moment with the temperature is expected. This is indeed the case also for $(\text{PcOs})_2$, which shows a marked temperature dependence of the magnetic moment ($0.56 \mu_B$ at 5 K). A plot of the experimental χ'_M values vs T (K) is given in Figure 5. The plot closely resembles that observed for $(\text{PcRu})_2$.^{1a} Owing to the structural similarities of $(\text{PcRu})_2$ and $(\text{PcOs})_2$, an approach to interpretation of the magnetic behavior of the osmium compound of the type developed for the ruthenium complex seemed reasonable. The marked increase of the χ'_M shown in Figure 5 at low temperatures suggests the presence of a paramagnetic impurity, a fact which is quite common with this type of materials. Within the reasonable assumption that the impurity follows the Curie law, a fitting was therefore attempted by the use of the expression

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

[where α is the mole fraction of the contaminant and χ_0 and χ_{imp} are the molar susceptibilities of $(\text{PcOs})_2$ and of the impurity, respectively] and of the expression for a clean paramagnet valid if the singlet state ($M_S = 0$) is assumed to lie lowest

$$\chi'_M = \frac{2Ng_{\text{eff}}^2\mu_B^2}{3k_B T} \left(\frac{e^{-x} + (2/x)(1 - e^{-x})}{1 + 2e^{-x}} \right)$$

where $x = D/k_B T$, g_{eff} is the effective gyromagnetic ratio, k_B is

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the Boltzmann constant, μ_B is the Bohr magneton, N is Avogadro's number, and T is the temperature (K).

The least-squares fitting of the experimental data leads to the values $\alpha = 0.02$, $g_{\text{eff}} = 1.7$, and $D = 507 \text{ cm}^{-1}$. The amount of impurity present (2%), lower than that found for $(\text{PcRu})_2$ (5.6%), is acceptable when considering the method of preparation of the complex. The higher D value obtained compared to that found for $(\text{PcRu})_2$ (235 cm^{-1}) is probably due to the expected larger spin-orbit coupling constant for Os(II) compared to that of Ru(II). Noticeably, the D value observed is close to that very recently found for $[(\text{OEP})\text{Os}]_2$ (630 cm^{-1}), the only alternative example of an Os(II)–Os(II) dimer magnetically investigated in detail.² The higher stabilization of the $M_s = 0$ state with respect to the $M_s = \pm 1$ states taking place for $[(\text{OEP})\text{Os}]_2$ and for $(\text{PcOs})_2$, as compared to that of their corresponding ruthenium analogues, is likely to explain the observed more consistent spin–spin coupling occurring for the Os species over all the temperature range explored. The good fitting of the present magnetic data fully confirms the expected behavior for the Os(II)–Os(II) couple within the dimer. In addition, it appears to exclude the presence of concurrent significant metal–metal interdimer magnetic contacts, in keeping with expectation, owing to the “encapsulated” location of the Os atoms within the dimer and the long interdimer Os–Os distance. The ruthenium dimer $(\text{PcRu})_2$ was previously assigned the electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$, which, indeed, should be more correctly reexpressed as $\sigma^2\pi^4\delta^{nb4}\pi^{*2}$, owing to the almost perfect staggered arrangement of the two Pc residues in the dimer. The twisted (30°) relative position of the two Pc skeletons in $(\text{PcOs})_2$, intermediate between staggered and eclipsed, makes uncertain the definitive assignment of the pertinent MO energy level sequence. Rigorously, splitting of the δ orbitals is expected in such a case (see, for instance, the

energy diagram given in ref 10, Figure 1b). On this basis, it appears that conclusive evidence is afforded for the assignment to $(\text{PcOs})_2$ of the energy level molecular orbital sequence $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$, which also accounts for a clean bond order 2 for the Os(II)–Os(II) couple. Finally, a nonmagnetic ground state pertains to the dimer as determined by the zero-field splitting of the $^3A_{2g}$ state.

Room-temperature electrical conductivity measurements on $(\text{PcOs})_2$ give a σ_{RT} value of $1 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$, coincident with that found for $(\text{PcRu})_2$. This suggests that some flow of charge is possible through the π contacts of the adjacent interdimer units within a single chain, as was the case for $(\text{PcRu})_2$, with no significant contribution for the contacts between parallel chains (Figure 3), as might be expected.

Conclusions. $(\text{PcOs})_2$ is the first example of an Os(II)–Os(II) dimer for which a combined structural and magnetic investigation has been developed.^{1b} Noteworthy, concomitantly with the publication of our data on $(\text{PcRu})_2$,¹ the hypothesis was advanced¹¹ that, in the light of the results on the dimeric Ru–Ru dimers already known, both ruthenium and osmium phthalocyanine could also be dimeric. Our previous¹ and present results fully confirm that hypothesis.

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