

Preparation, Structure, and Magnetic Properties of a Tetrakis(carboxylato)diosmium(III) Dichloride. Comparison with $\text{Os}_2(\text{hp})_4\text{Cl}_2$

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The compound $\text{Os}_2(2\text{-PBZ})_4\text{Cl}_2$, where 2-PBZ represents the 2-phenylbenzoate ion, has been synthesized by reaction of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with molten 2-phenylbenzoic acid, in 83% yield. The reddish-brown compound forms crystals in space group $P\bar{1}$, with $a = 11.552(2)$ Å, $b = 20.309(4)$ Å, $c = 10.907(2)$ Å, $\alpha = 100.44(2)^\circ$, $\beta = 116.57(1)^\circ$, $\gamma = 90.21(1)^\circ$, $V = 2248(1)$ Å³, and $Z = 2$. There are two independent centrosymmetric molecules with virtually identical structures and the following bond lengths: Os–Os = 2.3173(6), 2.3180(7) Å; Os–Cl = 2.386(3), 2.375(4) Å. The magnetic susceptibility has been measured from 1.5 to 304 K; the effective magnetic moment varies from 0.41 to 1.93 μ_B over this range. The data cannot be fitted either by a Bleaney–Bowers equation or to the behavior expected for a $^3A_{2g}$ state with zero-field splitting. It is therefore concluded that states arising from the $\sigma^2\pi^4\delta^2\delta^{*2}$, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^*$ and $\sigma^2\pi^4\delta^2\pi^{*2}$ configurations all play a role with strong spin–orbit coupling leading to a situation where neither the ground state nor the thermally accessible excited states can be specified with certainty. On the other hand, the magnetic properties of $\text{Os}_2(\text{hp})_4\text{Cl}_2$ can be satisfactorily explained by a zero-field-splitting model.

Introduction

Shortly after the first compound containing an Os_2^{6+} core, $\text{Os}_2(\text{hp})_4\text{Cl}_2$, was reported¹ the first carboxylate-bridged compounds, $\text{Os}_2(\text{O}_2\text{CR})_4\text{X}_2$, were described,² and a number of these are now known.^{3–5} Their chemistry has been further studied⁶ and some analogs with nitrogen-containing bridging ligands are known.^{7,8} The structures of three carboxylato compounds, namely the chlorides with $\text{R} = \text{CH}_3$, C_2H_5 , and C_3H_7 , have been determined by X-ray crystallography.^{4,5}

Since the $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ molecules contain two more electrons than the well-known $\text{Re}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ molecules,⁹ which have $\sigma^2\pi^4\delta^2$ quadruple bonds and $\delta \rightarrow \delta^*$ transitions at relatively low energies (they are the lowest singlet–singlet transitions), it would be natural to expect that the osmium compounds would have diamagnetic ground states derived from a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration. This would be analogous to the relationship between the $\text{W}_2\text{X}_4(\text{PR}_3)_4$ ($\sigma^2\pi^4\delta^2$) and $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ ($\sigma^2\pi^4\delta^2\delta^{*2}$) compounds.¹⁰ However, this is not what happens.

The $\text{Os}_2(\text{O}_2\text{CR})_4\text{X}_2$ compounds are all paramagnetic.^{4,5} On the other hand, the paramagnetism is less than that expected for two unpaired electrons and decreases with decreasing temperature, according to fragmentary studies in which measurements were made at only two temperatures, viz., ca. 300 K and ca. 190 K. An obvious, and, until now, tacitly accepted explanation for this

has been that there is indeed a singlet ground state derived from the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration, but that a thermally accessible triplet state derived from a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^*$ state gives rise to the temperature-dependent magnetic moment.

In an effort to test this hypothesis quantitatively, we have measured the magnetic susceptibilities of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ at closely spaced intervals from 300 K down to about 1.5 K. Unfortunately, because of its solubility properties and perhaps other unknown factors, we were never able to get a sample that was pure enough to give unambiguous results. It is quite common to find paramagnetic impurities giving rise to a steeply rising tail at very low temperatures in measurements such as these, but usually the quantity of impurity is small enough that a satisfactory correction can be made. In the case of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ the impurity level made it impossible to do so in an acceptable way.

Recently we found that the $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ compound with $\text{R} = 2\text{-phenylphenyl}$ is easy to recrystallize so as to obtain a very pure product. Moreover, with the rather large R group, the molecules are very well separated in the crystal so that intermolecular magnetic interactions should be negligible. We therefore characterized this compound structurally, to be sure it was not anomalous in any way, and then carried out a study of the temperature dependence of its magnetic susceptibility. Meanwhile we also investigated the magnetic behavior of the known complex $\text{Os}_2(\text{hp})_4\text{Cl}_2$ over a broad temperature range: 6–303 K.

Experimental Section

Standard vacuum-line Schlenk techniques were used to carry out the synthesis and the compound was subsequently handled under an argon atmosphere. All the solvents used were of reagent grade or better from commercial sources and freshly distilled under nitrogen from suitable drying reagents. The $\text{Os}_2(\text{hp})_4\text{Cl}_2$ was synthesized and purified according to the original preparation.¹ The $\text{Os}_2(\text{OAc})_4\text{Cl}_2$ was prepared according to Wilkinson's procedure.⁵ 2-Biphenylcarboxylic acid (98%) was purchased from Aldrich (under that name, but called by us 2-phenylbenzoic acid) and used without further purification.

$\text{Os}_2(2\text{-PBZ})_4\text{Cl}_2$. In a typical preparation, 0.21 g of $\text{Os}_2(\text{OAc})_4\text{Cl}_2$ (0.3 mmol) and 2.0 g of 2-phenylbenzoic acid (10 mmol) were heated at ca. 145 °C under an argon atmosphere for about 12 h. During the reaction period the acetic acid that formed was periodically distilled from the reaction system. The brown liquid was solidified by cooling to room

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Table I. Crystallographic Data for $\text{Os}_2(2\text{-BPZ})_4\text{Cl}_2$

chemical formula	$\text{Os}_2\text{Cl}_2\text{O}_8\text{C}_{52}\text{H}_{36}$
formula weight	1240.2
space group	$P\bar{1}$ (No. 2)
a , Å	11.552(2)
b , Å	20.309(4)
c , Å	10.907(2)
α , deg	100.44(2)
β , deg	116.57(1)
γ , deg	90.21(1)
V , Å ³	2248(1)
Z	2
d_{calc} , g cm ⁻³	1.838
$\mu(\text{Cu K}\alpha)$, cm ⁻¹	121.1
$\lambda(\text{Cu K}\alpha)$, Å	1.541 84
T , °C	20 ± 1
transm coeff: max, min	1.00, 0.29
R^a	0.055
R_w^b	0.078

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

temperature and subjected to 36 h of vacuum sublimation (≤ 0.05 Torr) at 110 °C to remove the excess 2-phenylbenzoic acid. Extraction of the dark residue with CH_2Cl_2 resulted in a brown solution, which was concentrated to ca. 25 mL and mixed with 50 mL of hexane. A brown homogeneous crystalline material which slowly precipitated from the CH_2Cl_2 -hexane mixture was filtered off and dried under vacuum. Yield: 0.31 g (83%). Anal. Calc: C, 50.31; H, 2.93. Found C, 49.7; H, 3.01. Single crystals suitable for the diffraction study were obtained by slow diffusion of hexane into the CH_2Cl_2 extract.

UV-vis (in CH_2Cl_2 ; nm ($\text{M}^{-1} \text{cm}^{-1}$)): 887 (53), 412 (8600), 296 (31 360). The cyclic voltammogram showed a reversible reduction at +602 mV, while ferrocene was oxidized at +715 mV under the same conditions.

Physical Measurements. The UV-visible spectra were recorded on a Cary 17D spectrometer at ambient temperature using a glass cell (900–400 nm) and a quartz cell (400–220 nm). Cyclic voltammetry measurements were carried out on a BAS 100 electrochemical analyzer in 0.1 M (*n*-Bu)₄NBF₄ solution (CH_2Cl_2) with a Pt working electrode and an Ag/AgCl reference electrode.

The variable-temperature magnetic susceptibility data were measured with an SHE 800 Series SQUID (superconducting quantum interference device) magnetometer at Michigan State University over the temperature ranges of 1.2–304 K for $\text{Os}_2(2\text{-PBZ})_4\text{Cl}_2$ and 6–303 K for $\text{Os}_2(\text{hp})_4\text{Cl}_2$ in applied fields of 5 kG (0.50 T) and 7 kG. The sample was loaded in a helium glovebox into a Kel-F bucket and then transferred to the instrument and loaded under a helium atmosphere. The sample was then rapidly cooled from room temperature to 5 K in zero field by loading it directly into the susceptometer and later also slowly cooled from 300 to 5 K in a field of 5 kG. No field dependence was observed, nor any difference in the susceptibility due to the two different thermal treatments of each sample. The numerical data are available as supplementary material.

X-ray Crystallography. A reddish brown parallelepiped of dimensions $0.37 \times 0.25 \times 0.05$ mm was mounted in a mixture of mineral oil and mother liquor in a Lindemann capillary. Indexing on 25 reflections in the 2θ range 48–55° gave a triclinic cell. The dimensions of the cell were confirmed by oscillation photographs. The data were collected on a Rigaku AFC5R diffractometer equipped with a Cu target. A detailed account of the normal crystallographic procedures we followed is presented elsewhere.¹¹ The data set was corrected for decay (–13%), Lorentz, and polarization effects. Empirical absorption corrections based on the ψ -scan method were applied to the data.¹² Both Os and Cl atoms were located by direct methods (SHELX-86). Other non-hydrogen atoms were then introduced by an alternating series of difference Fourier maps and least-squares refinements using the SDP package. All of the non-hydrogen atoms were refined with anisotropic thermal parameters to low residuals. A further difference Fourier map revealed that there were still about 10 peaks around the Os and Cl atoms (i.e. within 1.2 Å) with heights ranging from 3 to 0.8 $e/\text{Å}^3$. This is probably due to both the large absorption

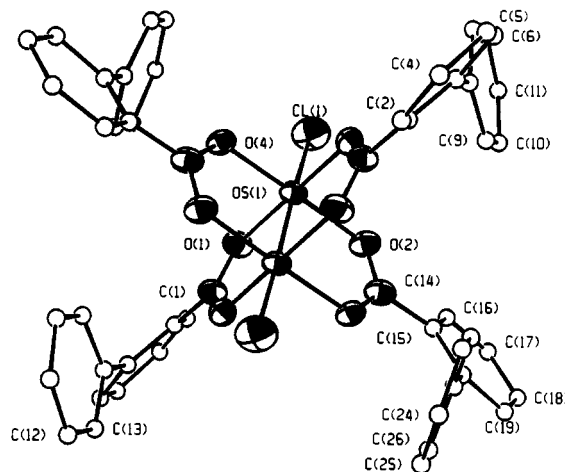


Figure 1. ORTEP drawing of the $\text{Os}_2(2\text{-PBZ})_4\text{Cl}_2$ molecule. All phenyl carbon atoms are represented as arbitrarily small circles for clarity. Important dimensions (Å or deg): Os–Os, 2.3173(6), 2.3180(7); Os–Cl, 2.386(3), 2.375(4); Os–O(av), 2.01[3]; Os–Os–O(av), 88.7[3]; Os–Os–Cl(av), 175.5[4].

effect for Cu K α radiation and an inexact correction based on the ψ -scan method for this particular thin plate. The final figures of merit are given in Table I.

Results and Discussion

An ORTEP drawing of one of the molecules is shown in Figure 1. The other one is very similar. The bond distances and angles are all normal, and a full list of bond angles is available in the supplementary material.

There are two crystallographically independent but effectively identical molecules each residing at an inversion center (0, 0, 0 and 0, 1/2, 0). The inner core of the molecule, $\text{Os}_2(\text{O}_2\text{C-})\text{Cl}_2$, has essentially D_{4h} symmetry. The mean Os–Os distance, 2.3176(5) Å is comparable to those previously found^{4,5} (2.314(1), 2.316(2), 2.301(1) Å). The mean Os–Cl distance, 2.381[5] Å, is just slightly below the range covered by the earlier structures, 2.417(3)–2.448(2) Å. On the whole, $\text{Os}_2(2\text{-PBZ})_4\text{Cl}_2$ may be considered an entirely representative $\text{Os}_2(\text{O}_2\text{CR})_4\text{X}_2$ compound.

The results of the magnetic measurements are presented graphically in Figure 2. This compound has slightly greater paramagnetism than those reported earlier ($\mu_{300} \approx 1.90 \mu_B$ vs $\sim 1.6 \mu_B$ and $\mu_{190} \approx 1.7 \mu_B$ vs $\sim 1.5 \mu_B$), but does not seem qualitatively different. Now that we have the temperature dependence clearly defined from 1.5 to 304 K, we tested the simple singlet–triplet model by seeing if the data can be fitted by a Bleaney–Bowers equation^{13a}

$$\chi = \frac{Ng^2\beta^2}{k_B T} \frac{2}{3 + \exp\left(-\frac{\Delta E}{k_B T}\right)} \quad (1)$$

with reasonable values of the adjustable parameters, g (the gyromagnetic ratio) and ΔE (the singlet–triplet separation). This does not appear to be possible, as shown in Figure 2, where the calculated curve shows one of the best “fits” possible.^{13b}

We must, therefore, consider other hypotheses to account for the magnetic properties of $\text{Os}_2(\text{O}_2\text{CR})_4\text{X}_2$ compounds. The possibility that such a compound has the δ^* orbital well above

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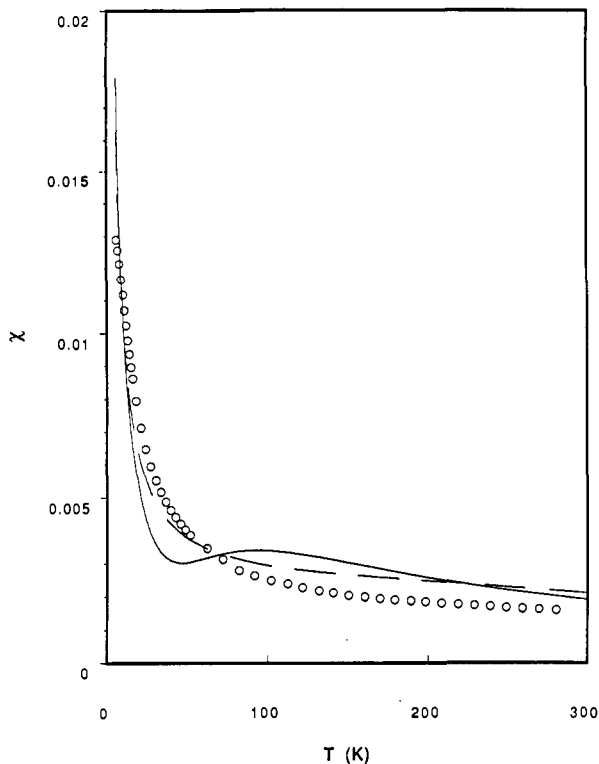


Figure 2. Magnetic susceptibility χ (emu) for $\text{Os}_2(2\text{-PBZ})_4\text{Cl}_2$ vs T (K), where the circles represent the measured data. The solid line and the dashed line are the best "fits" according to the Bleaney-Bowers model ($\Delta E = 133 \text{ cm}^{-1}$; $\alpha = 5.6\%$; $g = 1.802$) and the ZFS model ($D = 51 \text{ cm}^{-1}$; $\alpha = 4.4\%$; $g = 1.802$), respectively.

the π^* orbital, leading to a $\sigma^2\pi^4\delta^2\pi^{*2}$ configuration, and behavior like that of $\text{Os}_2((p\text{-tol})\text{NCHN}(p\text{-tol}))_4\text{Cl}_2$ ⁸ can be dismissed on structural grounds alone, since the presence of two π^* electrons would lead to an Os-Os bond length much greater than that found, probably $\geq 2.40 \text{ \AA}$. Nevertheless, we also tried to fit the data according to the zero-field-splitting (ZFS) model as follows

$$\chi = (1 - \alpha)\chi_0 + \alpha\chi_{\text{imp}} \quad (2)$$

where χ_{imp} is the contribution from a Curie-type $S = 3/2$ center and χ_0 is the zero-field-splitting susceptibility

$$\chi_0 = \frac{2Ng^2\beta^2}{3k_B T} \frac{e^{-x} + \frac{2}{x}(1 - e^{-x})}{1 + 2e^{-x}} \quad (3)$$

with $x = D/k_B T$ and D the zero-field-splitting. However, the fit also failed to converge, as can be seen from a "best fit" plotted in Figure 2. Thus the presence of a π^{*2} configuration to account for the susceptibility is not supported. Also, the shape of the experimental magnetic susceptibility curve is significantly different from that found for $\text{Os}_2((p\text{-tol})\text{NCHN}(p\text{-tol}))_4\text{Cl}_2$ and accounted for by the zero-field splitting of the $^3A_{2g}$ state arising from the π^{*2} configuration.⁸

Since neither of the two simple models just discussed provides, by itself, a satisfactory explanation, we make the following proposal. Because of a very small difference between the energies of states arising from the $\sigma^2\pi^4\delta^2\pi^{*2}$, $\sigma^2\pi^4\delta^2\delta^*\pi^*$ and $\sigma^2\pi^4\delta^2\pi^{*2}$ configurations and the large magnitude of spin-orbit coupling for osmium (see ref 8), we have in the $\text{Os}_2(\text{O}_2\text{CR})_4\text{X}_2$ molecules a complex situation in which there are several paramagnetic states lying only a few hundred wavenumbers above the lowest singlet state. However, we are not able to specify exactly what these states are, let alone develop parameterized equations that could be used to fit the experimental data. Furthermore, a close inspection of the three-dimensional packing diagram reveals extensive stacking among the phenyl rings of different molecules.

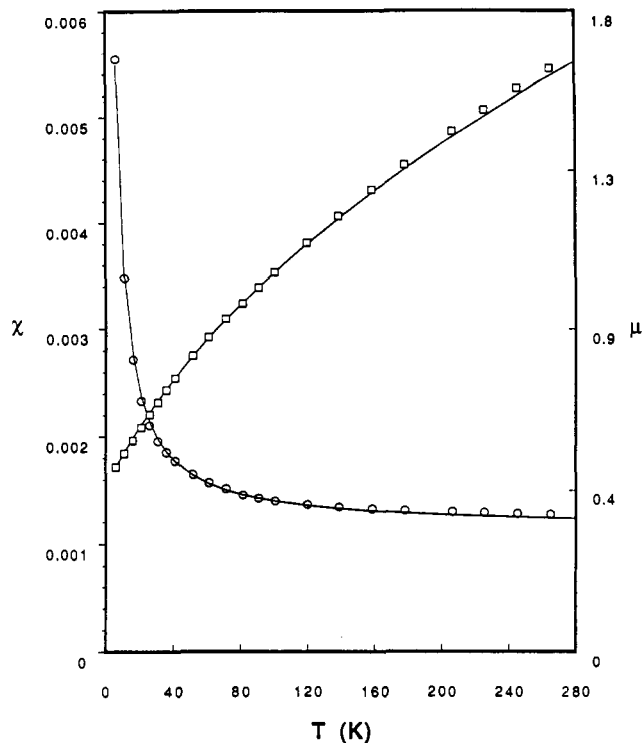


Figure 3. Overlay plots of the measured magnetic susceptibility χ in emu (O) and the effective moment μ in μ_B (□) for $\text{Os}_2(\text{hp})_4\text{Cl}_2$ with their corresponding theoretical fitting curves (solid lines) according to the ZFS model.

Such interactions might mediate weak ferro- or antiferromagnetic exchange through the lattice and cause the deviation from the standard model accounting for the isolated molecule. While this investigation can hardly be said to have had an entirely satisfactory outcome, it has had the positive virtue of eliminating two of the simpler schemes that might have been (and in one case definitely was) considered appropriate.

Magnetic and Electronic Structure of $\text{Os}_2(\text{hp})_4\text{Cl}_2$. The molar magnetic susceptibility (measured) and the corresponding effective magnetic moment are plotted in Figure 3. A nonlinear least-squares fit according to the ZFS model (eqs 2 and 3) converged with the following parameters: $g_{\text{eff}} = 1.922$, $D = 1196 \text{ cm}^{-1}$, and $\alpha = 1.4\%$. The adequacy of the ZFS model for $\text{Os}_2(\text{hp})_4\text{Cl}_2$ is obvious from the overlay plots of both fitted susceptibility and the corresponding moment (Figure 3). Therefore, it appears that the ground state electronic configuration in this case is $\sigma^2\pi^4\delta^2\pi^{*2}$, by the analogy to the established case of $\text{Os}_2(\text{DFM})_4\text{Cl}_2$.⁸ Additional support for a π^{*2} configuration comes from a relativistic SCF-X α calculation on the model complex $\text{Os}_2(\text{NHCHO})_4\text{Cl}_2$, which reveals an appreciable HO-MO(π^*)-LUMO(δ^*) gap of 0.355 eV .¹⁴

It is worthwhile to mention the distinction between the diosmium(III) and diruthenium(II) systems. Previously it was found that while both $\text{Ru}_2(\text{DFM})_4$ and the analogous complex $\text{Ru}_2(\text{triazenate})_4$ have a π^{*4} ground-state configuration,¹⁵ $\text{Ru}_2(\text{O}_2\text{CR})_4$ as well as $\text{Ru}_2(\text{xhp})_4$ display magnetic behavior that is fully consistent with a $\pi^{*2}\delta^2\pi^{*2}$ configuration.^{16,17} A decisive factor is the subtle influence of the π -basicity of the two coordinated atoms of the bridging ligands. For the diosmium(III)

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complexes, both formamidinate and hydroxypyridinate have a π^{*2} configuration, while for the carboxylate, we have concluded that this is a mixture of the configurations π^{*2} and $\pi^*\delta^*$. Since the comparison between diruthenium(II) and diosmium(III) is based on an identical set of bridging ligands, the different outcome can only be attributed to the inherent differences of the metal centers. Two major factors are the greater positive charge on the diosmium(III) unit and the increased relativistic effects from Ru to Os. The former results in a significant downshift of d-block orbitals on Os, and hence a stronger $\pi(L)-\delta^*$ interaction. The second factor, on the other hand, will generally result in an upshift of both d and f shells due to the contraction of both s and p shells,¹⁸ and a reduction of the $\pi^*(L)-\delta^*$ interaction is expected.

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Apparently the former overrides the latter, and a larger $\pi(L)-\delta^*$ interaction (in other words, an effectively greater π -basicity for a ligand bound to Os(III) than for one bound to Ru(II)) becomes a general feature for the diosmium systems. A more quantitative analysis would require more sophisticated calculations, beyond the Hartree-Fock level.

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Supplementary Material Available: Complete tables of crystallographic procedural data, positional parameters, bond angles, and thermal displacement parameters and lists of magnetic susceptibilities at various temperatures (15 pages). Ordering information is given on any current mathead page.