

Preparation and Structure of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ and Theoretical Investigation of $\text{Cu}(\text{pc})(\text{ReO}_4)$, $\text{Cu}(\text{pc})(\text{ReO}_4)_2$, and $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$

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Abstract: The compound $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ (pc = phthalocyaninato) has been prepared by electrocrystallization from a *p*-dichlorobenzene solution of Cu(pc) and $[\text{N}(n\text{-Bu})_4][\text{ReO}_4]$. $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ crystallizes with one formula unit in the triclinic space group $P\bar{1}$ with cell constants at $T = 153$ K of $a = 12.6202(6)$ Å, $b = 13.7596(7)$ Å, $c = 14.0294(7)$ Å, $\alpha = 64.6376(9)^\circ$, $\beta = 64.2570(9)^\circ$, and $\gamma = 66.0549(9)^\circ$. The molecular structure comprises a stack of three Cu(pc) rings; the Cu center in each peripheral ring has an attached ReO_4 ligand, the Cu–O distance being 2.374(5) Å. The inter-ring distance is 3.1595(11) Å. Density functional theory calculations for $\text{Cu}(\text{pc})(\text{ReO}_4)$ and $\text{Cu}(\text{pc})(\text{ReO}_4)_2$ suggest that the ring- π states are the source of the electron donation to the ligands. Calculations for $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ suggest that the charges on the central and peripheral rings are nearly equal. For all three compounds the basic spin distributions are similar to each other and to those of other Cu(pc) systems. For $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ a localized, rather than an itinerant, description of the magnetism is indicated.

Introduction

Partially oxidized porphyrinic compounds, many of which exhibit metallic conductivity, normally adopt structures in which there are one-dimensional stacks of macrocyclic rings, with these stacks separated from one another by anions.^{1,2} Such compounds may be described as charge-transfer salts. A wide range of compositions is known, including compounds of the type $(\text{M}(\text{p}))_3(\text{A})_2 \cdot \text{S}$ (M = metal, p = macrocycle; A = anion; S = solvent). However, a few $(\text{M}(\text{p}))_n(\text{A})_m$ molecular compounds have been discovered.^{3–5} One example is $\text{Cu}(\text{pc})(\text{ReO}_4)$ (pc = phthalocyaninato), a singly ring-oxidized M(p) compound. It crystallizes with two formula units in the asymmetric unit and possesses two five-coordinate Cu centers; the Cu–O(ReO_3) bond lengths are 2.440(4) and 2.451(5) Å; another example is $\text{Cu}(\text{pc})(\text{ReO}_4)_2$, a doubly ring-oxidized M(p) compound with a six-coordinate Cu center and Cu–O bonds 2.526(5) Å in length.⁵ Here we present another example, namely the new compound $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ whose structure comprises not the expected infinite one-dimensional stacks of pc rings separated by anions, but molecules consisting of stacks of three Cu(pc) rings with each peripheral ring being ligated by a ReO_4 ligand. We also present the results of density functional theory calculations for

all three compounds, namely $\text{Cu}(\text{pc})(\text{ReO}_4)$, $\text{Cu}(\text{pc})(\text{ReO}_4)_2$, and $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$.

Experimental Section

Materials. $\text{H}_2(\text{pc})$ was prepared and purified by a literature method.⁶ $[\text{N}(n\text{-Bu})_4][\text{ReO}_4]$ (Aldrich) was purified by sublimation. *p*-Dichlorobenzene (Aldrich) was used without further purification. Cu(pc) was synthesized by metalation of $\text{H}_2(\text{pc})$ through the use of dehydrated $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99.9999%).⁷

$(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$. Crystals of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ grew at the anode of an electrolytic cell. The cell comprised two arms separated by a porous glass frit. The electrolyte, $[\text{N}(n\text{-Bu})_4][\text{ReO}_4]$ (0.120 g), was added to each arm of the cell. Cu(pc) (0.031 g) was added to the anode compartment. *p*-Dichlorobenzene (24.5 g) was added to each compartment. Platinum electrodes were inserted into the cell. The cell was immersed in a 123(2) °C oil bath, protected from light, and purged with dry N_2 . Although all of the electrolyte dissolved, not all of the Cu(pc) did. The tendency of the molten *p*-dichlorobenzene to sublime was minimized by periodically heating the upper parts of the arms of the cell. A 0.5 μA current was applied to the cell for two months when small prismatic crystals of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ were harvested from the surface of the anode. Semiquantitative energy dispersive analysis with X-rays (EDX) verified the presence of Cu and Re.

X-ray Crystallography. X-ray diffraction data from a single crystal of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ were collected on a Bruker SMART 1000 CCD diffractometer with the use of graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Data were collected by an ω scan of 0.25° in groups of 727 frames each at φ settings of 0°, 90°, 180°, and 270°, followed by 50 more frames at $\varphi = 0^\circ$ to determine the extent of

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Table 1. Crystallographic Data for $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$

compound	tri(phthalocyaninatocopper(II))diperrhenate
empirical formula	$\text{C}_{96}\text{H}_{48}\text{Cu}_3\text{N}_{24}\text{O}_8\text{Re}_2$
formula wt, amu	2228.60
a , Å	12.6202(6)
b , Å	13.7596(7)
c , Å	14.0294(7)
α , deg	64.6376(9)
β , deg	64.2570(9)
γ , deg	66.0549(9)
V , Å ³	1909.22(16)
T , K	153(2)
Z	1
ρ_{calc} , g/cm ³	1.938
space group	$P\bar{1}$
radiation	Mo $K\alpha$, $\lambda = 0.71073$ Å
μ , cm ⁻¹	40.65
R_1^a	0.0526
wR_2^b	0.1201

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o^2 > 2\sigma F_o^2$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$ for all data; $w^{-1} = \sigma^2(F_o^2) + (0.04 F_o^2)^2$ for $F_o^2 \geq 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Table 2. Numerical Atomic Orbital Basis

atom	core	valence
Re	1s...5s	5p,d 6s,p
Cu	1s...3p	3d, 4s,p
O	1s	2s,p 3s,p
N	1s	2s,p 3s,p
C	1s	2s,p 3s,p
H		1s

possible crystal decay. The exposure times were 30 s/frame. Intensity data were collected with the program SMART.⁸ Cell refinement and data reduction were carried out with the use of the program SAINT,⁸ face-indexed absorption corrections were carried out with the program XPREP,⁹ and the frame variations were further corrected with the use of the program SADABS.⁸ The structure was solved with the direct methods program SHELXS and refined with the least-squares program SHELXL of the SHELXTL-PC suite of programs.⁹ The final refinement included anisotropic displacement parameters. The positions of the hydrogen atoms were fixed by geometry ($\text{C}-\text{H} = 0.95$ Å) and were not varied. Further details are provided in Table 1 and in the Supporting Information.

Density Functional Theory Calculations. A variational expansion of the one-electron wave functions and energies was obtained by expansion in a numerical atomic/ionic basis, with the use of the Discrete Variational Method^{10–12} within the framework of Density Functional Theory (DFT). The basis atoms/ions can be optimized to give a compact and efficient representation of the molecular states. In the present calculations the bases were partially optimized, using averages of the self-consistent Mulliken atomic orbital populations to define effective atomic configurations. The partially optimized numerical atomic orbital basis sets used in the variational wave function expansions are given in Table 2. Numerical integration/sampling sets of 300–1000 points per atom were generated to calculate the Density Functional Hamiltonian and overlap matrix elements. The Coulomb and exchange-correlation potentials were evaluated in the so-called Self-Consistent Multipolar procedure, which makes use of least-squares expansions of the charge and spin density with controlled precision. Convergence of energies to better than 0.001 eV and of density expansion coefficients

to ~ 0.0001 e were found to be adequate here. The standard self-consistent-field (SCF) matrix secular equations were solved iteratively until the desired level of convergence in charge and spin densities was obtained. We characterize the present expansions as near-minimal, capable of describing general features of the electronic charge and spin distributions. It is possible to generate states of well-defined spin projection value M_S in the present method, and this permits us to explore important low-lying excitations as well as the relative stability of a given SCF solution.

Since the structures of $\text{Cu}(\text{pc})(\text{ReO}_4)$, $\text{Cu}(\text{pc})(\text{ReO}_4)_2$, and $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ consist of isolated molecules rather than extended stacks, we expect the nature of their electronic interactions to differ from those of the stacked oxidized phthalocyanines.^{13,14} Two types of charge analysis were performed for each compound to verify this expectation. First, the traditional Mulliken atomic orbital population analysis of the occupied orbitals was used to extract effective atomic configurations. Second, volume-analysis was performed, involving a partition of the space associated with each atom and an integration of the charge and spin density within each volume. The Mulliken method is more chemically intuitive, whereas the volume-integration method is more attuned to concepts of ionic and covalent atomic radii. Neither scheme is unique: the Mulliken method depends on the definition of basis sets whereas the volume-integration method depends on the definition of atomic volumes. However, the combination of the two methods leads to considerable insight into the charge and spin distributions. We have calculated the charge and spin distributions of the isolated molecular unit, without taking into account interactions with the neighboring (neutral) molecular units.

Results

Structure of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$. The crystal structure of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ consists of the packing of $\text{Cu}(\text{pc})_3(\text{ReO}_4)_2$ molecules. Each molecule, which possesses a crystallographically imposed center of symmetry, comprises a stack of three $\text{Cu}(\text{pc})$ rings with each outer ring bonded to a ReO_4 ligand through a $\text{Cu}-\text{O}$ bond. Figure 1 displays the molecule and Table 3 provides selected bond lengths and angles.

The Cu atom of the central ring is at the center of symmetry, and hence is in the least-squares plane of the pc ring. This ring is essentially planar with a mean absolute deviation from the plane of the 24-atom core of 0.007(4) Å and a maximum deviation of 0.079(8) Å for a peripheral benzene C atom. Each outer ring is slightly bowed (mean deviation, 0.022(11) Å; maximum deviation, 0.188(7) Å for a peripheral benzene C atom), as can be discerned in Figure 1. The Cu atom of the outer pc ring is displaced 0.134(1) Å in the direction of the perrhenate O atom; the $\text{Cu}-\text{O}$ distance is 2.374(5) Å, significantly shorter than in $\text{Cu}(\text{pc})(\text{ReO}_4)$ and $\text{Cu}(\text{pc})(\text{ReO}_4)_2$ (see Table 3). The inner and outer $\text{Cu}(\text{pc})$ units are staggered by 40.3° and their least-squares planes make an angle of 0.47(10)° with one another. The inter-ring distance of 3.1595(11) Å (defined as the distance from the Cu atom of the central ring to the 24-atom least-squares plane of the outer ring) is significantly shorter than that in $\text{Cu}(\text{pc})\text{I}$ (3.195(4) Å),¹⁵ suggesting that charge may be able to flow along the stacking direction of the molecule.

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Table 3. Comparison of Averaged Selected Distances (Å) and Angles (deg) in Cu(pc)(ReO₄), Cu(pc)(ReO₄)₂, and (Cu(pc))₃(ReO₄)₂^a

quantity	Cu(pc)(ReO ₄) ₂	Cu(pc)(ReO ₄)	Cu(pc) ₃ (ReO ₄) ₂	
			outer pc	central pc
Cu—O	2.526(5)	2.446(8)	2.374(5)	
Cu—N _p	1.967(8)	1.958(9)	1.949(5)	1.947(5)
N _p —C _a	1.37(3)	1.373(14)	1.372(8)	1.374(7)
N _m —C _a	1.33(2)	1.337(14)	1.335(8)	1.328(8)
C _a —C _b	1.458(9)	1.455(15)	1.454(9)	1.461(8)
C _b —C _b	1.399(11)	1.401(16)	1.396(8)	1.397(8)
C _b —C _c	1.391(10)	1.392(8)	1.389(9)	1.393(8)
C _c —C _d	1.392(10)	1.392(6)	1.381(9)	1.387(9)
C _d —C _d	1.400(9)	1.398(9)	1.392(15)	1.380(9)
Re—O	1.73(3)	1.73(2)	1.71(3)	
Cu-plane ^b	0	0.094(3)	0.1344(13)	0
mean deviation from plane	0.025(16)	0.03(3)	0.022(11)	0.007(4)
max. deviation from plane	0.082(8)	0.24(10)	0.188(7)	0.079(8)
N _p —Cu—N _p	90.0(6)	89.9(3)	89.8(2)	90.0(2)
C _a —N _p —Cu	126.5(8)	126.4(9)	126.4(4)	126.0(4)
C _a —N _p —C _a	107.0(9)	107.1(5)	107.1(5)	108.0(5)
C _a —N _m —C _a	126(3)	124(2)	122.6(5)	122.1(7)
N _m —C _a —N _p	125(2)	126.7(1.8)	127.3(6)	127.9(7)
N _p —C _a —C _b	111(2)	110.4(1.1)	110.2(5)	109.4(7)
N _m —C _a —C _b	123.9(4)	123.0(1.0)	122.5(5)	122.7(5)
C _c —C _b —C _a	132.8(7)	132.6(1.5)	132.7(9)	131.9(6)
C _b —C _b —C _a	106(2)	106.1(1.2)	106.3(6)	106.6(5)
C _b —C _b —C _c	121.3(1.1)	121.3(1.5)	121.0(9)	121.5(6)
C _d —C _c —C _b	117.4(9)	117.3(7)	117.6(8)	116.7(7)
C _c —C _d —C _d	121.3(7)	121.4(3)	121.4(7)	121.8(8)
N _p —Cu—O	90.0(1.0)	92(4)	94(3)	
Cu—O—Re	127.7(3)	127.3(2), 139.0(2)	138.0(2)	

^a The error estimate in parentheses of a given quantity is equal to the larger of the standard deviation of a single observation as estimated from the group or of the largest estimated standard deviation of a group member. ^b Plane = 24-atom plane of the pc core.

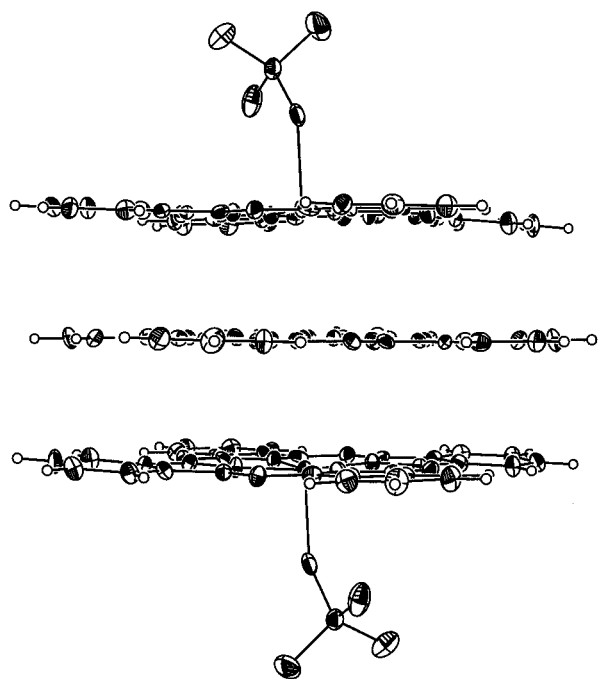


Figure 1. A view of the Cu(pc)₃(ReO₄)₂ molecule parallel to the pc planes. Displacement ellipsoids are drawn at the 50% probability level.

Figure 2 shows a space-filling view of [Cu(pc)(ReO₄)] portions of adjacent (Cu(pc))₃(ReO₄)₂ molecules. The ReO₄ groups of each layer appear to act as bumpers, positioning the

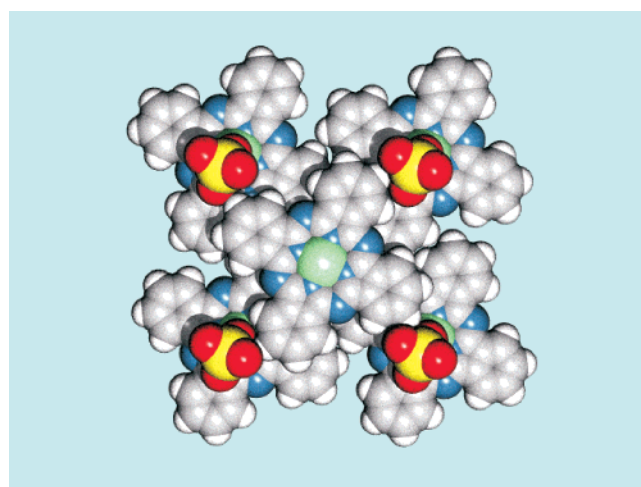


Figure 2. Space-filling view²⁶ of overlapping portions of Cu(pc)₃(ReO₄)₂.

next layer of molecules. A peripheral benzene ring of the outer Cu(pc) unit of one molecule overlaps the meso region of another molecule at an interplanar distance of 3.284(6) Å.

DFT Charge Distributions. The Mulliken atomic orbital analyses of charge and spin density for Cu(pc)(ReO₄), Cu(pc)-

Table 4. Mulliken Atomic Orbital Analyses of Charge and Spin Density

molecule	group	charge	spin
$\text{Cu}(\text{pc})(\text{ReO}_4)$	Cu	1.596	0.279
	CuN_8^a	-6.465	0.575
	$\text{Cu}(\text{pc})$	0.817	0.501
	ReO_4	-0.816	-0.002
$\text{Cu}(\text{pc})(\text{ReO}_4)_2$	Cu	1.563	0.249
	CuN_8	-5.948	0.511
	$\text{Cu}(\text{pc})$	1.975	0.417
	ReO_4	-0.987	0.041
$(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ (AF)	Cu (central)	1.395	-0.360
	CuN_8	0.524	-0.774
	$\text{Cu}(\text{pc})$	0.558	-0.635
	Cu (peripheral)	1.516	0.271
	CuN_8	0.487	0.537
	$\text{Cu}(\text{pc})$	0.658	0.553
	ReO_4	-0.937	0.015

^a CuN_8 refers to the summed charge and spin associated with the Cu atom and eight N atoms of each moiety.

Table 5. Volume-Integrated Atomic Charge and Spin Densities

molecule	group	charge	spin
$\text{Cu}(\text{pc})(\text{ReO}_4)$	Cu	2.278	0.278
	CuN_8	0.532	0.504
	$\text{Cu}(\text{pc})$	0.797	0.502
	ReO_4	-0.796	-0.002
$\text{Cu}(\text{pc})(\text{ReO}_4)_2$	Cu	2.344	0.249
	CuN_8	0.708	0.446
	$\text{Cu}(\text{pc})$	1.624	0.420
	ReO_4	-0.811	0.040
$(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ (AF)	Cu (central)	2.165	-0.352
	CuN_8	0.335	-0.655
	$\text{Cu}(\text{pc})$	0.533	-0.641
	Cu (peripheral)	2.350	0.263
	CuN_8	0.481	0.485
	$\text{Cu}(\text{pc})$	0.642	0.555
	ReO_4	-0.909	0.016

$(\text{ReO}_4)_2$, and $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ are presented in Table 4 and the volume-integrated atomic charge and spin densities are given in Table 5.

Calculations from the isolated $\text{Cu}(\text{pc})$ molecule¹³ suggest that electrons will be withdrawn primarily from the diffuse “ a_u ” ring- π orbitals. For $\text{Cu}(\text{pc})(\text{ReO}_4)$ and $\text{Cu}(\text{pc})(\text{ReO}_4)_2$, this was verified by EPR spectroscopy.⁵

For $\text{Cu}(\text{pc})(\text{ReO}_4)$, the Cu atomic configuration, according to Mulliken analysis, is $\text{Cu}^{1.60} 3d^{9.16} 4s^{0.11} 4p^{0.14}$. The ReO_4 moiety is somewhat less than fully ionized; the summed charge on the (ReO_4) group is -0.816 e (Mulliken) and -0.796 e (volume-integrated). That the O atom bonded to the Cu atom ($\text{Cu}-\text{O} = 2.374(5) \text{ \AA}$) has an increased charge (-1.023 e Mulliken, -1.98 e volume) relative to the remaining three O atoms (-0.82 e Mulliken, -1.74 e volume) is evidence of mixed covalent and ionic bonding.

For $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$, with nearly two electrons withdrawn from $\text{Cu}(\text{pc})$, we find the Cu configuration to be only slightly altered compared with $\text{Cu}(\text{pc})(\text{ReO}_4)$: $\text{Cu}^{1.56} 3d^{9.13} 4s^{0.10} 4p^{0.20}$. This supports the expectation that the ring- π states are the source of both donated electrons. The Cu volume charge of 2.34 e shows that less than 0.1 e has been removed from the $\text{Cu}(\text{pc})$ core in the second “ionization” caused by the ReO_4 ligands. The Mulliken charge of the ReO_4 moiety is -0.987 e, whereas its volume charge of -0.81 e is slightly but significantly increased compared with that in $\text{Cu}(\text{pc})(\text{ReO}_4)$.

We can imagine two extreme possibilities for the $(\text{Cu}(\text{pc}))_3$ -

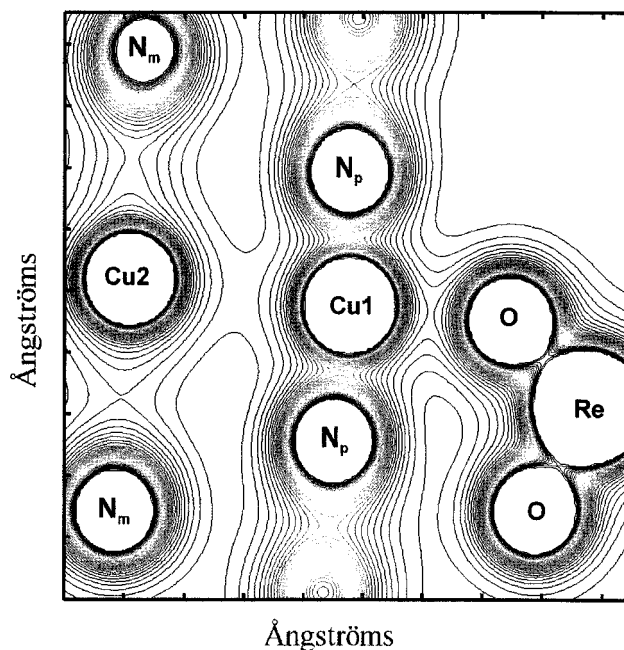


Figure 3. Charge density map of the Cu1–Cu2–Re plane of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$. The Cu atom of the outer $\text{Cu}(\text{pc})$ ring is denoted “Cu1”; that of the central $\text{Cu}(\text{pc})$ ring is denoted “Cu2”. This view includes two pyrrole N atoms (denoted “ N_p ”) bound to Cu1 and the O atom binding the ReO_4 group to Cu1. Contours are equal-interval, spaced at 0.0081 e/a.u.^2 .

(ReO_4)₂ molecule: a uniform charge withdrawal from each pc ring or a neutral central ring and one-electron charged outer rings each bonded to an O atom of a ReO_4 ligand. Both Mulliken and volume-based charge analyses predict that the actual configuration lies between these extremes, but much closer to the uniform-charge model. The effective configuration for the central Cu atom is $\text{Cu}^{1.40} 3d^{9.17} 4s^{0.15} 4p^{0.28}$ whereas that of the peripheral Cu atom is $\text{Cu}^{1.52} 3d^{9.09} 4s^{0.13} 4p^{0.26}$, which indicates slightly greater metal ionicity for the ion directly bonded to the O atom of the ReO_4 ligand. The corresponding volume charges of 2.18 and 2.35 e, respectively, confirm this tendency, as do the net $\text{Cu}(\text{pc})$ volume charges of 0.54 and 0.64 e, respectively. Thus ~0.1 e more is withdrawn from the peripheral $\text{Cu}(\text{pc})$ rings compared with the central one. The ReO_4 volume charge of -0.91 e is less than that in either $\text{Cu}(\text{pc})(\text{ReO}_4)$ or $\text{Cu}(\text{pc})(\text{ReO}_4)_2$, perhaps indicating a greater stability of the highly delocalized electronic states of the three-layer $\text{Cu}(\text{pc})$ stack. Examination of charge density maps (Figure 3) reveals that the actual shared bond charge of the Cu–O bond is small compared with that in the shorter Cu–N bond.

DFT Spin Distributions. As is found in isolated $\text{Cu}(\text{pc})$ and related porphyrin derivatives,^{16–18} the majority of the spin density resides on the Cu atoms, with considerable delocalization (~30%) onto the nearest-neighbor pyrrole N atoms. For $\text{Cu}(\text{pc})(\text{ReO}_4)$, $\text{Cu}(\text{pc})(\text{ReO}_4)_2$, and $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ we find the basic spin distributions to be very similar to each other and to those of other $\text{Cu}(\text{pc})$ systems. That is, whereas the π -electron distribution is sufficiently strongly coupled in the $\text{Cu}(\text{pc})$ stack of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ to allow charge mobility, the spin distributions are sufficiently localized to be characterized as weakly

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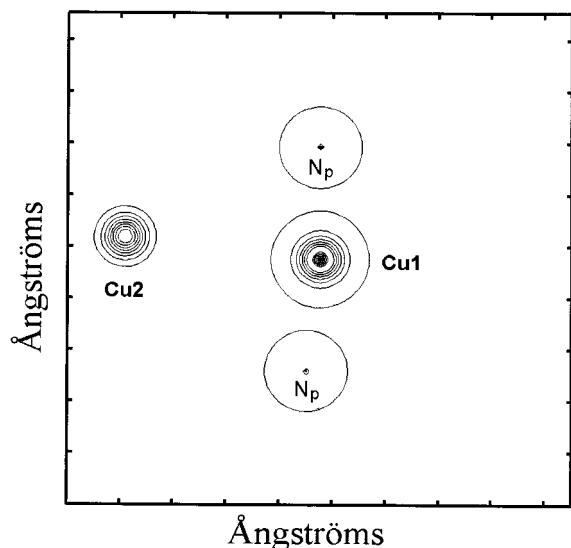


Figure 4. Projection of the $M_s = 1/2$ spin density of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ onto spherically symmetric functions about each atomic center in equal-interval contours ($0.0209 \text{ e}/\text{au}^2$) onto the plane of Figure 3. The O and Re atoms do not appear because there is no spin density on them.

interacting. Thus localized, rather than itinerant, descriptions of magnetism are indicated.

$\text{Cu}(\text{pc})(\text{ReO}_4)$ is predicted to display singlet or triplet spin structures arising from coupling of the unpaired CuN_4 and ring- π spins. The EPR results agree with this prediction, suggesting a triplet state formed by exchange coupling of a d^9 Cu center and pc π -radical.⁵ We have examined the spin distributions by “scanning” the SCF states as a function of M_s ; in every case the Cu-pyrrole core retains its well-defined spin structure, and the diffuse ring states merely adapt to the imposed net spin state.

For $\text{Cu}(\text{pc})(\text{ReO}_4)_2$ we would expect the removal of two “ a_u ” electrons to reduce the spin distribution back to the CuN_4 doublet, and EPR results confirm that this is the ground state.⁵ We have again explored the stability of magnetic structures by performing a series of SCF calculations for different M_s values.

Both ferromagnetic (F: all Cu spins parallel) and antiferromagnetic (AF: central Cu reversed) spin configurations of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ were investigated and found to be stable. The charge distribution and energy levels are only slightly different in the two magnetic states. The Cu-centered spin distributions are dominated by the $d_{(x^2-y^2)}$ local orientation in each plane and are hence anisotropic. To display the extent of spin polarization over the entire molecule, we show in Figure 4 a projection of spin density onto spherically symmetric functions about each center. To estimate the magnetic coupling energy between the Cu spins, we performed Magnetic Transition State (MTS) calculations on the molecule.^{19,20} Here we report the simplest result, that of a spin-flip on the central Cu atom, for which the AF configuration is found to be more stable, with an energy difference of 0.11 eV. This may be taken as a first approximation to the energy difference between $S = 3/2$ and $1/2$ states of the system. It would be desirable to carry out experimental studies of the magnetic properties of this system, but sufficient material is not available. However, an EPR study of a sample of five crystals of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ at 9 GHz (X band) showed an anisotropic signal at the threshold of detectability at 77 K.²¹

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Discussion

NMR evidence suggests that doubly charged aggregates of three porphyrinic units are particularly stable²² and several other porphyrinic compounds with a ring-to-anion ratio of 3 to 2 are known.^{23–25} To the best of our knowledge, all of these compounds possess columns of stacked macrocycles in their extended structures. The packing of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ as discrete molecules rather than as stacks was thus unexpected.

As mentioned above, the Cu–O bond distance in $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ is significantly shorter than those in $\text{Cu}(\text{pc})(\text{ReO}_4)_2$ and $\text{Cu}(\text{pc})(\text{ReO}_4)$ (Table 3). The Cu– N_p bonds of the central and outer $\text{Cu}(\text{pc})$ rings of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ are possibly shorter than the analogous ones in $\text{Cu}(\text{pc})(\text{ReO}_4)_2$ (Table 3). The Re–O–Cu angle varies widely among these compounds, presumably reflecting differing intermolecular interactions. Consistent with the conclusions from the DFT analysis, there are no significant differences in the symmetry-averaged bond lengths and angles of the phthalocyanine rings in $\text{Cu}(\text{pc})(\text{ReO}_4)$, $\text{Cu}(\text{pc})(\text{ReO}_4)_2$, and $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$.

The CuN_4 pyrrole core shows itself to be highly stable in both charge and spin distributions. The addition of a fifth or sixth oxygen-bonded ligand produces only minor changes in the Cu configuration. The electronic states of the trimer $\text{Cu}(\text{pc})$ stack of $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ are found to be highly delocalized; nearly equal amounts of charge are transferred from central and peripheral components. The net charge of the monovalent ReO_4 group is close to unity; a small but significant reduction in ionicity is noted in the sequence $\text{Cu}(\text{pc})(\text{ReO}_4)_2$, $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$, $\text{Cu}(\text{pc})(\text{ReO}_4)$. The $S = 1/2$ magnetic distributions associated with the CuN_4 complex can couple with the singly occupied ring- π states, and with each other in the layered compound. The relatively weak coupling can be described with the use of a Magnetic Transition State scheme; the $S = 1/2$ to $3/2$ spin-flip energy for $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ is found to be 0.11 eV.

The intermolecular distance of 3.284(6) Å in $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ is shorter than the plane–plane distance in the semiconductor $\text{Co}(\text{pc})(\text{CN})_2 \cdot 2\text{CHCl}_3$ (3.5–3.6 Å). This compound, whose powder resistivity is $\sim 10^2 \Omega$ at room temperature, conducts by means of the overlap of peripheral benzene rings.³ This suggests the possibility in $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ of electronic conduction via π -overlap from one molecule to another in an excited state.

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Supporting Information Available: Crystallographic data for $(\text{Cu}(\text{pc}))_3(\text{ReO}_4)_2$ in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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