83665-05-8; [(TPP)Cr(py)$_2$]$^+$, 83665-06-9; [(TPP)Cr(3-CH$_3$-py)$_2$]$^+$, 83665-07-0; [(TPP)Cr(4-CH$_3$-py)$_2$]$^+$, 83665-08-1; [(TPP)Cr(3,4-(CH$_3$)$_2$-py)$_2$]$^+$, 83665-09-2; (TPP)Cr(3,5-Cl$_2$-py)$_2$, 83665-10-5; (TPP)Cr(3-CN-py)$_2$, 83665-11-6; (TPP)Cr(4-CN-py)$_2$, 83665-12-7; (TPP)Cr(3-Cl-py)$_2$, 83665-13-8; (TPP)Cr(3-Cr-py)$_2$, 83665-14-9; (TPP)Cr(3-COCH$_3$-py)$_3$, 83665-15-0; (TPP)Cr(4-COCH$_3$-py)$_2$, 83665-16-1; (TPP)Cr(py)$_2$, 67113-84-2; (TPP)Cr(3-CH$_3$-py)$_2$, 67113-85-3; (TPP)Cr(4-CH$_3$-py)$_3$, 67113-86-4; (TPP)Cr(3,4-(CH$_3$)$_2$-py)$_2$, 83665-17-2; (TPP)CrCl(3,5-Cl$_2$-py), 81329-11-5; (TPP)CrCl(3-CN-py), 81329-12-6; (TPP)CrCl(4-CN-py), 65013-14-1; (TPP)CrCl(3-Cl-py), 81329-13-7; (TPP)CrCl(3-Br-py), 81329-14-8; (TPP)CrCl(3-COCH$_3$-py), 81329-15-9; (TPP)CrCl(py), 65013-13-0; (TPP)CrCl(3-CH$_3$-py), 81329-17-1; (TPP)CrCl(4-CH$_3$-py), 81329-18-2; (TPP)CrCl(3,4-(CH$_3$)$_2$-py), 65013-15-2; [(TPP)Cr(3,5-Cl$_2$-py)$_2$]$^-$, 83665-19-4; [(TPP)Cr(3-CN-py)$_2$]$^-$, 83665-20-7; [(TPP)Cr(3-Cl-py)$_2$]$^-$, 83665-21-8; [(TPP)Cr(3-Cr-py)$_2$]$^-$, 83665-22-9; [(TPP)Cr(3-COCH$_3$-py)$_2$]$^-$, 83665-23-0; [(TPP)Cr(py)$_2$]$^-$, 83665-24-1; [(TPP)Cr(3-CH$_3$-py)$_2$]$^-$, 83665-25-2; [(TPP)Cr(4-CH$_3$-py)$_2$]$^-$, 83665-26-3; [(TPP)Cr(3,4-(CH$_3$)$_2$-py)$_2$]$^-$, 83665-27-4; EtCl$_2$, 107-06-2; CH$_2$Cl$_2$, 75-09-2; PhCN, 100-47-0; PrCN, 109-74-0; (CH$_3$)$_2$CO, 67-64-1; THF, 109-99-9; DMF, 68-12-2; DMA, 127-19-5; Me$_2$SO, 67-68-5; py, 110-86-1.

Notes

Contribution from the Department of Energy and Environment,
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Structural Consequences of Oxidation in Photosynthetic Models. Crystal Structure of (Perchlorato)-(5,10,15,20-tetraphenylporphinato)magnesium(II)

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The primary photochemical reactions in plant and bacterial photosynthesis consist of the transfer of an electron, in a picosecond time domain, from (bacterio)chlorophyll phototraps to nearby acceptors to yield (bacterio)chlorophyll π cation radicals.[1] Although structural investigations have provided detailed geometries for (bacterio)chlorophylls and their derivatives,[2–4] similar studies of the oxidized species have been precluded so far by the instability of the radicals, particularly their tendency to undergo oxidative dehydrogenations. As a model of the structural and stereochemical consequences of the loss of an electron in the photosynthetic chromophores, we present here an X-ray determination of a magnesium porphyrin radical, (perchlorato)(5,10,15,20-tetraphenylporphinato)magnesium(II) (**1**), MgTPP$^{+}\cdot$ClO$_4^-$.[5]

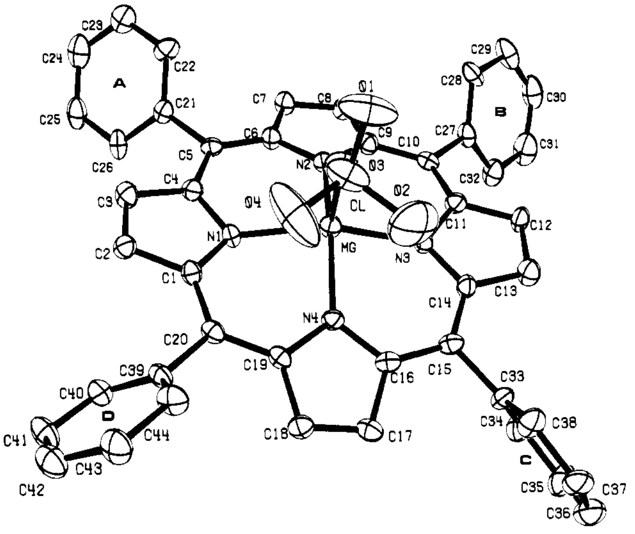

Figure 1. The structure of **1** and atom-numbering system. The thermal ellipsoids are drawn to enclose 50% probability. Hydrogen atoms have been omitted for clarity.

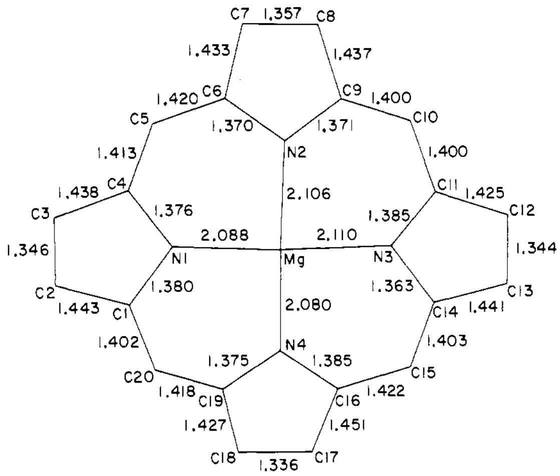

Figure 2. Bond distances (Å) for the core of **1**. The esd is 0.005 Å for a typical Mg–N bond and 0.008 Å for a C–C bond.

The molecular structure of **1** and atom names are shown in Figure 1. (Experimental details are given in Table I, and fractional coordinates for the non-hydrogen atoms are presented in Table II.) Bond distances for the core of the macrocycle are displayed in Figure 2. The C$_\alpha$–N, C$_\beta$–C$_\beta$, C$_\alpha$–C$_\beta$, C$_\alpha$–C$_m$, and C$_m$–C$_{Ph}$ distances average 1.376 (3), 1.346 (4), 1.437 (3), 1.410 (3), and 1.493 (4) Å, respectively. They agree well with the corresponding bond lengths in MgTPP(H$_2$O),[9] although the latter exhibits a fourfold symmetry. They are also consonant with those found in chlorophyllides (Chl) a[2] and b[3] and in the cation radical ZnTPP$^{+}\cdot$ClO$_4^-$,[7] and with the

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(1) (a) Fajer, J.; Fujita, I.; Davis, M. S.; Forman, A.; Hanson, L. K.; Smith, K. M. *Adv. Chem. Ser.* **1982**, *No. 201*, 489. (b) Davis, M. S.; Forman, A.; Hanson, L. K.; Thornber, J. P.; Fajer, J. *J. Phys. Chem.* **1979**, *83*, 3325 and references therein.

(2) (a) Chow, H. C.; Serlin, R.; Strouse, C. E. *J. Am. Chem. Soc.* **1975**, *97*, 7230. (b) Kratky, C.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1586.

(3) Serlin, R.; Chow, H. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1975**, *97*, 7237.

(4) Barkigia, K. M.; Fajer, J.; Smith, K. M.; Williams, G. J. B. *J. Am. Chem. Soc.* **1981**, *103*, 5890.

(5) The radical was generated electrochemically at 0.6 V (vs. SCE) in dichloromethane containing 0.1 M tetrapropylammonium perchlorate as electrolyte[6] and isolated as described by Spaulding et al.[7] In solution, **1** exhibits optical and electron spin resonance spectra characteristic of $^2A_{2u}$ radicals.[6,8]

(6) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451.

(7) Spaulding, L. D.; Eller, P. G.; Bertrand, J. A.; Felton, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 982.

(8) Fajer, J.; Borg, D. C.; Forman, A.; Felton, R. H.; Vegh, L.; Dolphin, D. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 349.

(9) Timkovich, R.; Tulinsky, A. *J. Am. Chem. Soc.* **1969**, *91*, 4430.

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Table I. Crystallographic Details for $C_{44}H_{28}N_4MgClO_4$

Crystal Data

unit cell, space group: monoclinic, $P2_1/c$
$V = 3555.0$ Å^3
$Z = 4$
$M_r = 736.5$
$a = 13.825$ (1) Å[a]
$b = 13.076$ (1) Å
$c = 20.639$ (1) Å
$\beta = 107.67$ (1)°
density calcd: 1.38 g/cm^3
cryst descripn: tiny reddish prism, 0.06 × 0.10 × 0.16 mm

Data Collection

diffractometer: Enraf-Nonius CAD4
radiation: Cu Kα, $\lambda = 1.54$ 18 Å, graphite monochromated
linear abs coeff: 15.33 cm^{-1} (analytical absorption corrections calculated by using the program ABSOR[b] with the correction ranging from 1.08 to 1.18)
2θ range: $0° \leqslant 2\theta \leqslant 120°$
no. of reflcns: 11 733 reflcns measd ($\pm h,k,\pm l$); 5557 unique, 2687 having $F_o > 2\sigma(F_o)$[c]
scattering factors: Cromer and Mann;[d] Stewart, Davidson, and Simpson[e]
anomalous dispersion: Cromer and Liberman[f]
solution and refinement: starting coordinates taken from $ZnTPP^+ \cdot ClO_4^-$ with which 1 is isomorphous; model refined anisotropically in two matrix blocks against 2687 data having $F_o > 2\sigma(F_o)$
R_F $(= \Sigma |F_o - F_c| / \Sigma |F_o|)$: 0.067
R_{wF} $(= (\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2)^{1/2})$: 0.066

[a] The figure in parentheses is the estimated standard deviation of the least significant figure here and throughout the paper. [b] All programs are described in: "Brookhaven National Laboratory, Chemistry Department, CRYSNET Manual", Informal Report BNL 21714; Berman, H. M., Berstein, F. C., Bernstein, H. J., Koetzle, T. F., Williams, G. J. B., Eds.; Brookhaven National Laboratory: Upton, NY, 1976. [c] The quantities F_o and F_c are the observed and calculated structure amplitudes, w is the experimental weight, where $w^{-1} = \sigma^2_c + (0.04F_o)^2$, and σ^2_c is the variance from counting statistics. [d] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* 1968, *A24*, 321. [e] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, *42*, 3175. [f] Cromer, D. T.; Liberman, D. J. *Ibid.* 1970, *53*, 1891.

Table II. Final Positional Parameters (×10^4) for the Non-Hydrogen Atoms of 1

atom	x	y	z
CL	2561(1)	2568(2)	-992(1)
MG	2486(2)	1020(2)	187(1)
O1	3287(4)	2989(5)	-1247(3)
O2	2271(7)	3395(6)	-577(5)
O3	2993(3)	1804(3)	-483(2)
O4	1674(6)	2283(7)	-1424(3)
N1	1785(3)	-213(4)	-417(2)
N2	3721(3)	51(3)	645(2)
N3	2956(3)	1904(4)	1083(2)
N4	1045(3)	1643(4)	9(2)
C1	875(4)	-157(5)	-931(3)
C2	834(5)	-946(5)	-1428(3)
C3	1697(5)	-1490(5)	-1202(3)
C4	2289(4)	-1043(5)	-570(3)
C5	3245(4)	-1399(5)	-162(3)
C6	3873(4)	-911(5)	432(3)
C7	4762(5)	-1366(5)	890(3)
C8	5130(5)	-670(5)	1393(3)
C9	4485(5)	215(5)	1239(3)
C10	4594(4)	1086(5)	1647(3)
C11	3913(5)	1905(5)	1555(3)
C12	4024(5)	2799(5)	1966(3)
C13	3148(5)	3324(5)	1768(3)
C14	2477(5)	2753(4)	1216(3)
C15	1448(5)	2982(5)	910(3)
C16	770(4)	2437(5)	362(3)
C17	-319(5)	2595(5)	110(3)
C18	-678(5)	1921(5)	-392(3)
C19	156(4)	1333(4)	-460(3)
C20	106(4)	548(5)	-943(3)
C21	3588(5)	-2411(5)	-348(3)
C22	4524(5)	-2525(5)	-443(3)
C23	4851(5)	-3465(6)	-595(4)
C24	4226(7)	-4304(6)	-650(4)
C25	3298(6)	-4201(5)	-562(4)
C26	2976(5)	-3273(5)	-405(3)
C27	5499(5)	1122(5)	2272(3)
C28	6474(5)	1070(5)	2224(3)
C29	7307(5)	1108(6)	2816(4)
C30	7160(6)	1180(6)	3441(4)
C31	6204(6)	1212(7)	3488(4)
C32	5374(5)	1187(6)	2912(4)
C33	974(4)	3791(5)	1217(3)
C34	860(6)	3655(6)	1852(4)
C35	346(7)	4334(6)	2111(4)
C36	-110(5)	5185(6)	1731(4)
C37	36(5)	5366(6)	1124(4)
C38	579(5)	4663(6)	867(3)
C39	-867(5)	471(5)	-1510(3)
C40	-1374(5)	-436(5)	-1680(3)
C41	-2254(5)	-531(6)	-2211(3)
C42	-2651(6)	314(7)	-2580(4)
C43	-2179(6)	1240(6)	-2431(3)
C44	-1277(5)	1321(5)	-1894(3)

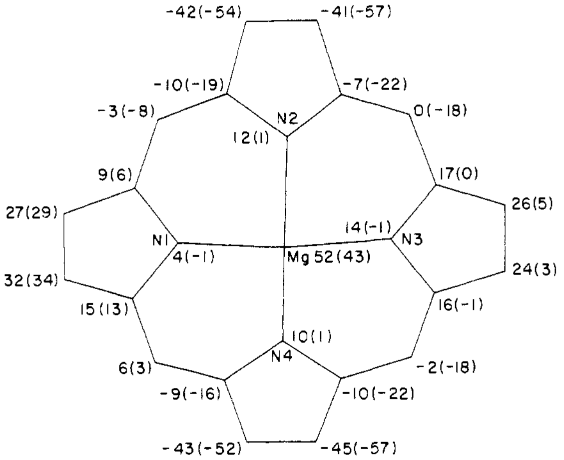

Figure 3. Deviations (Å × 10^2) from the least-squares plane of the macrocycle and, in parentheses, from the plane of the four nitrogens. The average uncertainty in a nitrogen displacement is 0.005 Å.

average distances calculated by Hoard[10] from an analysis of 16 different porphyrin structures (Table III). Bond angles, provided as supplementary material, show similarly good agreement.

Individually, the pyrrole rings are planar to 0.01 Å, but as a whole, the macrocycle is quite distorted (Figure 3) with the largest displacements (~-0.4 Å) occurring at the C_β positions of rings II and IV and somewhat smaller deviations (~0.3 Å) at the β atoms of rings I and III. This alternate up and down cant of the pyrrole rings results in a ruffling of the skeleton. While these deviations are comparable to those in $ZnTPP^+ \cdot ClO_4^-$, they are larger, on the average, by 0.20 Å than the analogous distortions in (pyridine)(tetrapyridylporphinato)zinc(II) (pyZnTPyP).[11] This increased nonplanarity may be caused by coordination of the perchlorate ion with the porphyrin bending in order to minimize nonbonding interactions. Here, and in $ZnTPP^+ \cdot ClO_4^-$ and $Fe^{III}TPP^+ \cdot ClO_4^-$,[12] two of the uncoordinated oxygen atoms (O2 and O4) lie symmetrically on either side of N4 with the macrocycles assuming pronounced S_4 symmetries. In contrast, in (perchlorato)(octaethylporphinato)iron(III),[13] the porphyrin is flat but one oxygen lies nearest to a meso carbon and another rests above a C_α–N bond.

In 1, the Mg–O3 distance is very short, 2.012 (5) Å, and comparable to the M–O bond of 2.029 (4) Å found[12] in $Fe^{III}TPP^+ClO_4^-$. By comparison, the M–O bonds in $MgTPP(H_2O)$[9] and hydrated ethyl chlorophyllides *a*[2a] and *b*[3] are 2.072 (1), 2.035 (6), and 2.012 (7) Å. Thus, substitution of perchlorate for water as an axial ligand does not appear to greatly perturb the Mg–O bond. (The larger deviation from the Mg–O distance in $MgTPP(H_2O)$ may be due in part to

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(10) Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: New York, 1975; p 317.

(11) Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3761.

(12) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.

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Table III. A Comparison of Distances (Å) in 1 with Those in Similar Porphyrins

	this work	mean of 16 studies[10]	EtChl*a*[2a]	EtChl*b*[3]	$MgTPP(H_2O)$[9]
C_α-N	1.376 (3)[a]	1.379 (6)	1.374 (7)	1.369 (11)	1.376 (10)[b]
C_β-C_β	1.346 (4)	1.354 (10)	1.370 (17)[c]	1.365 (6)[c]	1.360 (10)
C_α-C_β	1.437 (3)	1.443 (5)	1.448 (10)[c]	1.441 (5)[c]	1.431 (10)
C_α-C_m	1.410 (3)	1.390 (11)	1.389 (10)	1.398 (5)	1.415 (10)
C_m-C_{Ph}	1.493 (4)	1.499 (5)			1.540 (10)

[a] $\sigma_m = (\Sigma_m(l_m - l)^2/m(m-1))^{1/2}$, where l_m is the mean bond length, l is the measured length, and m is the number of measurements. [b] If only two measurements, σ_m was taken as the mean of the two individual σ's. [c] Based on unsaturated rings only.

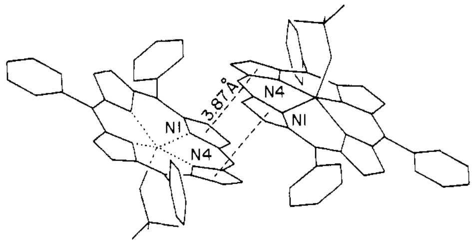

Figure 4. View of the molecular packing that illustrates the overlap of ring I with ring IV of an inversion-related molecule. Phenyl ring D attached to C20 has been removed for clarity. Another representation of this interaction with all four phenyl groups intact has been included with the supplementary material.

the uncertainty in the *z* coordinate of the Mg in that structure.[9,10])

The coordination of the magnesium[14] in the porphyrin pocket is somewhat asymmetric (~6σ differences in distances) with the metal pushed toward rings I and IV at lengths of 2.088 (5) and 2.080 (5) Å and away from II and III at 2.106 (5) and 2.110 (5) Å. These lie in the range found[2,3] in chlorophyllides *a* and *b* of 2.004 (9)–2.101 (9) Å and compare with the sole Mg–N distance of 2.072 (10) Å observed[9] in $MgTPP(H_2O)$.

A feature of the present structure is the close molecular packing in which rings I and IV of inversion-related molecules overlap with a perpendicular separation of 3.87 (1) Å between ring centers, indicative of weak π–π interactions (Figure 4). (Weak aggregates of $ZnTPP^{+\cdot}$[6] and $MgTPP^{+\cdot}$[8] have also been postulated to exist in solution in order to rationalize electron spin resonance data.) Such close intermolecular contacts, normally considered unlikely because of steric hindrance by the phenyl groups, may account for the observed twists of those rings. They are attached to the meso carbons at significantly acute dihedral angles of 47.3 (3), 55.4 (3), 63.2 (3), and 42.1 (3)° for rings A–D, respectively. However, in at least two other nonradical porphyrins, ZnTPyP[11] and $Fe^{III}TPP^+ClO_4^-$,[12] the meso aryl rings are far from perpendicular to the porphyrin plane.

In conclusion, these results, and those previously reported for $ZnTPP^{+\cdot}ClO_4^-$,[7] suggest that the porphyrin π system acts as a sink and that abstraction of an electron to yield a π cation induces no major effects on the bond distances and stereochemistry of the macrocycle (with the possible exception of the ruffling, which may accommodate the counterion). Extrapolation of these data to (bacterio)chlorophyll cation radicals in vivo suggests that the structural invariance assumed by the Franck–Condon principle[15] holds true not only during the actual electron transfer but also for the initial and final conformational states of the chromophores.[16] This minimal nuclear rearrangement may thus also favor[15] the rapid electron transfer observed in the primary charge separation of photosynthetic organisms.[1]

In a different context, these results further indicate that the common usage of neutral-molecule coordinates for molecular orbital calculations of porphyrin radicals[1,6] should not introduce significant errors.

Acknowledgment. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016. We thank the Chemistry Department at BNL for use of the diffractometer.

Registry No. 1, 83731-60-6.

Supplementary Material Available: Listings of structure amplitudes, selected bond angles, distances and angles in the phenyl rings, some least-squares planes, anisotropic thermal parameters for the nonhydrogen atoms, fractional coordinates for the hydrogen atoms, and distances in the perchlorate bound to Mg and a view of the molecular packing with all four phenyl rings attached to both molecules (22 pages). Ordering information is given on any current masthead page.

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(14) At the request of a reviewer, the following bond angles are presented here rather than in the supplementary material: N1–Mg–N2 = 88.3 (1)°, N1–Mg–N4 = 87.2 (2)°, N2–Mg–N3 = 86.8 (2)°, N3–Mg–N4 = 87.9 (2)°; N1–Mg–O3 = 100.3 (2)°, N2–Mg–O3 = 102.2 (2)°, N3–Mg–O3 = 104.2 (2)°, N4–Mg–O3 = 101.2 (2)°; Mg–O3–Cl = 134.5 (3)°.

(15) Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. B., Sutin, N., Eds. "Tunneling in Biological Systems"; Academic Press: New York, 1979.

(16) Reduced porphyrins, i.e., chlorins, bacteriochlorins, and isobacteriochlorins, exhibit a wide range of conformations because of the flexibility of the reduced pyrrole rings.[2,3,4,17] Obviously, the present porphyrin study does not allow an assessment of the effects of oxidation on the conformations of the reduced rings of (bacterio)chlorophyll radicals.

(17) Barkigia, K. M.; Fajer, J.; Chang, C. K.; Williams, G. J. B. *J. Am. Chem. Soc.* **1982**, *104*, 315 and references therein.

Contribution from the School of Chemical Sciences,
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Electron-Transfer Reactions of Tetrakis(μ-acetato)dirhodium(II) and the Self-Exchange Rate of the $Rh_2(OAc)_4^+/Rh_2(OAc)_4$ Couple

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and Roderick D. Cannon*

Received May 24, 1982

The binuclear rhodium(II) complexes of the type $Rh_2(OOCR)_4X_2$ (R = alkyl; X = H_2O and various other donors) have been shown to undergo one-electron oxidation.[1-3] The complex $Rh_2(OAc)_4(OH_2)_2^+$ has the same structure[4] as the corresponding reduced species[5] but with significantly shorter Rh–Rh and Rh–O bonds. Photoelectron,[6] vibrational,[2,7] and

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(1) C. R. Wilson and H. Taube, *Inorg. Chem.*, **14**, 2276 (1975).

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(3) M. Moszner and J. J. Ziolkowski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **24**, 433 (1976); *Chem. Abstr.*, **85**, 153239*q* (1976).

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(5) F. A. Cotton, B. G. De Boer, M. D. La Prade, J. R. Pipal, and D. A. Ucko, *Acta Crystallogr., Sect. B*, **B27**, 1664 (1971).

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