TABLE I

PERIODATE OXIDATIONS

Compound		0.25	0.75	1.5	3	7	24	48
					Time, hr.			
1-Amino-2,6-anhydro-1-deoxy-D-*glycero*-L-*manno*-heptitol (III)	Uptake	3.02	3.47	3.74	3.98	4.21	4.51	4.86[a]
	Acid	0.48	0.78	0.47	1.14	1.37	1.67	2.24[a]
2,6-Anhydro-1-deoxy-1-(2,4-dinitrophenylamino)-D-*glycero*-L-*manno*-heptitol (VI)	Uptake	1.68	1.81	1.84	1.88	1.92	1.98	2.01
	Acid	0.59	0.72	0.78	0.80	0.82	0.87	0.89
2,6-Anhydro-D-*glycero*-L-*manno*-heptitol (VIII) hemihydrate	Uptake	1.59	1.70	1.80	1.90	1.98	2.00	2.01
	Acid	0.41	0.49	0.55	0.61	0.66	0.73	0.76

[a] At 102 hr.

Anal. Calcd. for $C_{19}H_{28}O_{12}$ (448.41): C, 50.89; H, 6.29; Ac, 57.60. Found: C, 50.85; H, 6.52; Ac, 57.36.

1-**Deoxy**-D-*glycero*-L-*gluco*-**heptitol** (**XI**).—A sample (0.59 g.) of the hexaacetate XII was deacetylated with barium methoxide to give from ethanol 0.151 g. of clusters of needles, m.p. 138–149°. Repeated recrystallization of this material failed to remove a minor impurity (R_f 0.69 in solvent system A); the mixture was therefore chromatographed on a sheet of Whatman No. 31 paper (extra thick) in solvent system A. After deionization, the eluate was concentrated and the residue crystallized from ethanol as clusters of needles (0.156 g., 60%), m.p. 148–149° (preliminary sintering), unchanged by two recrystallizations from ethanol. The material showed $[\alpha]^{20}D$ −2° in water (c 2.94), $[\alpha]^{20}D$ −45° in acidified ammonium molybdate (c 0.38), and R_f 0.33 in system B; infrared peak: ν_{max}^{Nujol} (cm.$^{-1}$) 3285 s (OH).

Anal. Calcd. for $C_7H_{16}O_6$ (196.20): C, 42.85; H, 8.22; C–CH$_3$, 13.79. Found: C, 43.04; H, 8.17; C–CH$_3$ (Kuhn–Roth), 13.52.

The same substance was also made through the reductive desulfurization of D-*glycero*-L-*gluco*-heptose diethyl dithioacetal[8] with Raney nickel.

Oxidations with Periodate.—Oxidations with sodium metaperiodate in unbuffered solution were carried out using conventional techniques; the results, expressed in moles of oxidant consumed and moles of formic acid produced per mole of substrate, are listed in Table I.

COMMUNICATIONS TO THE EDITOR

The Electronic Structures of Square-Planar Metal Complexes. IV. A Square-Planar Rhodium(II) Complex[1]

Sir:

The reaction between anhydrous rhodium(II) acetate, disodium maleonitriledithiolate (Na₂MNT), and (*n*-C₄H₉)₄NOH in methanol yields a red solution and a green crystalline precipitate. Analytical and conductance data established that the formula of the green solid is [(*n*-C₄H₉)₄N]₂[Rh(MNT)₂]. The X-ray powder diffraction pattern of the complex shows it to be isomorphous and presumably isostructural with [(*n*-C₄H₉)₄N]₂[Ni(MNT)₂]. Since Ni(MNT)₂$^{-2}$ is known to be truly square-planar[2] a square-planar structure (I) for Rh(MNT)₂$^{-2}$ is established.
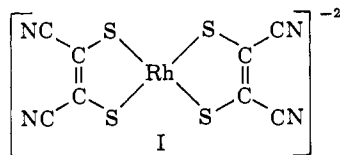
The pertinent data are given in Table I.

Although there has been a revival of interest in the complex chemistry of rhodium, most of the work has been on Rh(III)[3] and Rh(I),[4] and to date there has been no report of a well-characterized, mononuclear complex of Rh(II).[5,6] The Rh(MNT)₂$^{-2}$ complex is

(1) The support of the National Science Foundation and the National Institutes of Health is gratefully acknowledged. We thank Dr. James Bolton for help with the e.s.r. measurements and Dr. Susan A. Johnson for a sample of Rh₂(OAc)₄.

(2) R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 113 (1964).

(3) (a) S. A. Johnson, F. Basolo, and R. G. Pearson, *ibid.*, **85**, 1741 (1963); (b) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962), and references therein.

(4) See for example, S. S. Bath and L. Vaska, *J. Am. Chem. Soc.*, **85**, 3500 (1963), and references therein.

TABLE I

COMPARISON OF THE [(*n*-C₄H₉)₄N]₂[Rh(MNT)₂] AND [(*n*-C₄H₉)₄N]₂[Ni(MNT)₂] COMPLEXES

Complex	X-Ray[a]	Λ[b]	μ_{eff}, B.M.	E.s.r.
[(*n*-C₄H₉)₄N]₂-[Rh(MNT)₂][c]	12.28, 9.71, 8.85, 7.90, 7.25, 6.87, 6.15, 5.04, 4.90, 4.50, 4.21, 3.77, 3.62, 3.45, 3.10	150	1.91	g_1 = 1.950, g_2 = 2.015, g_3 = 2.35
[(*n*-C₄H₉)₄N]₂-[Ni(MNT)₂]	12.12, 9.70, 8.93, 7.83, 7.20, 6.11, 5.04, 4.88, 4.50, 4.17, 3.77, 3.72, 3.45, 3.12	165	Diamagnetic	...

[a] Interplanar spacings (Å.) of the most prominent peaks. [b] For 0.0001 *M* nitromethane solutions at 25°, expressed in cm.² mole^{-1} ohm.$^{-1}$. [c] *Anal.* Calcd. for $C_{40}H_{72}N_6S_4Rh$: C, 55.33; H, 8.36; N, 9.48. Found: C, 55.52; H, 8.74; N, 9.68.

the first reported example of a square-planar complex of rhodium(II).

The magnetic moment of solid [(*n*-C₄H₉)₄N]₂[Rh(MNT)₂] is 1.91 B.M. The e.s.r. spectrum of polycrystalline [(*n*-C₄H₉)₄N]₂[Rh(MNT)₂] is shown in Fig. 1. The three g values obtained are: g_1 = 1.950, g_2 = 2.015, g_3 = 2.35. The three-line spectrum is very similar to the frozen solution spectra obtained for the electronically similar Ni(TDT)₂$^-$, Ni(MNT)₂$^-$,

(5) There are several examples of diamagnetic Rh(II) complexes, which presumably are binuclear. See, for example (a) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963); (b) B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nucl. Chem.*, **23**, 207 (1961).

(6) The structure of Rh(py)₄I₂, reported by F. P. Dwyer and R. S. Nyholm [*J. Proc. Roy. Soc. N. S. Wales*, **76**, 275 (1943)], is not known.

Fig. 1.—Electron spin resonance spectrum of polycrystalline $[(n\text{-}C_4H_9)_4N]_2[Rh(MNT)_2]$.

$Pd(MNT)_2^-$, and $Pt(MNT)_2^-$ complexes, which have $S = \frac{1}{2}$.[7,8] From the e.s.r. and static susceptibility results, we conclude that the square-planar $Rh(MNT)_2^{-2}$ complex has a spin-doublet ground state. To our knowledge, this is the first well-characterized mononuclear, paramagnetic rhodium(II) complex.[15]

The ground state of $Rh(MNT)_2^{-2}$ is $\ldots(4b_{2g})^2 (4a_g)^1 = {}^2A_g$, using the molecular orbitals derived[2] for $Ni(MNT)_2^{-2}$. The low energy ligand-to-$4a_g$ charge-transfer band is located at 15,800 cm.$^{-1}$ ($\epsilon \cong 4000$) in $Rh(MNT)_2^{-2}$. All the planar complexes mentioned above with a ${}^2A_g$ ground state show this type of low energy charge-transfer band.

(7) In frozen DMF–CHCl₃ solutions, the following g values have been obtained[9]: Ni(MNT)₂⁻, $g_1 = 1.996$, $g_2 = 2.043$, $g_3 = 2.140$; Pd(MNT)₂⁻, $g_1 = 1.956$, $g_2 = 2.046$, $g_3 = 2.065$; Pt(MNT)₂⁻, $g_1 = 1.825$, $g_2 = 2.067$, $g_3 = 2.221$; these complexes have $S = \frac{1}{2}$. Solid $[(n\text{-}C_4H_9)_4N][Ni(TDT)_2]$ shows only two lines, with $g_\perp = 9.045$ and $g_\parallel = 2.193$.[10] However, the in-plane anisotropy is resolved in solid $[(C_6H_5)As(CH_3)][Ni(TDT)_2]$, with $g_1 = 2.020$, $g_2 = 2.075$, $g_3 = 2.130$.[11] In a frozen DMF–CHCl₃ solution Ni(TDT)₂⁻ gives $g_1 = 2.011$, $g_2 = 2.043$, $g_3 = 2.181$.[12] The anion Ni(TDT)₂⁻ was the first reported example of a nickel complex with a square-planar structure and a spin-doublet ground state.[10]

(8) It is interesting to note that Co(MNT)₂⁻², for which both spin-quartet[13] and spin-doublet[14] ground states have been proposed, has a considerably different g_3 from that of $[(n\text{-}C_4H_9)_4N]_2[Rh(MNT)_2]$, which is a spin-doublet; for a single crystal of 5% $[(n\text{-}C_4H_9)_4N]_2[Co(MNT)_2]$ in $[(n\text{-}C_4H_9)_4N]_2[Ni(MNT)_2]$, the values $g_1 = 1.977$, $g_2 = 2.025$, and $g_3 = 2.798$ have been reported.[14]

(9) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).

(10) H. B. Gray and E. Billig, *ibid.*, **85**, 2019 (1963).

(11) I. Bernal, unpublished results.

(12) We thank Dr. N. Edelstein for measuring this spectrum for us.

(13) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(14) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 3049 (1963).

(15) There are very few paramagnetic rhodium compounds of any structural type. Paramagnetic Rh(IV) fluorides have been reported by R. S. Nyholm and A. G. Sharpe, *J. Chem. Soc.*, 3579 (1952).

(16) (a) NIH Postdoctoral Fellow, 1963–1964; (b) NSF Graduate Fellow, 1963–1964.

DEPARTMENT OF CHEMISTRY   E. BILLIG
COLUMBIA UNIVERSITY   S. I. SHUPACK[16a]
NEW YORK, NEW YORK 10027   JAMES H. WATERS
                                           RAYMOND WILLIAMS[16b]
                                           HARRY B. GRAY
RECEIVED JANUARY 2, 1964

The Triclinic Crystal Form of α,β,γ,δ-Tetraphenylporphine[1]

Sir:

A recent X-ray structure determination of tetraphenylporphine[2] does not distinguish between pyrrole rings with and without hydrogen attached to nitrogen, since the tetragonal space group requires 4 molecular symmetry. Since fourfold symmetry is higher than the molecule permits, it may either be inexact or the result of molecular disorder within the crystal. The X-ray analysis of a triclinic tetraphenylporphine[3] crystal, space group P1, avoids the above difficulties because of lower, 1, molecular symmetry and thus distinguishes two types of pyrrole rings and the two central hydrogen atoms. Results of this analysis are reported here.

Deviations from a least-squares plane determined by the 24 atoms of the porphine nucleus are given in Fig. 1.
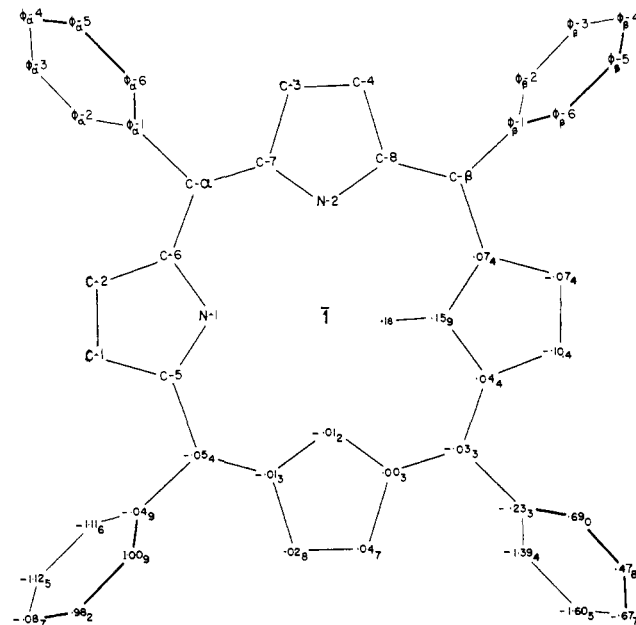

Fig. 1.—Atomic nomenclature and deviations in Å. from the nuclear least-squares plane of triclinic tetraphenylporphine.

Of note are (1) the tilt (6.6°) of the N-1 pyrrole ring, which makes the close central hydrogen–hydrogen contact ~0.2 Å. longer than a planar configuration allows; (2) the tilt (9.1°) of the C-α–(C₆H₅)$_\alpha$-4 line with respect to the plane, for which a close (3.40 Å.) intermolecular contact may account; and (3) the rotation of the phenyl groups ((C₆H₅)$_\alpha \sim 61.0°$, (C₆H₅)$_\beta \sim 63.1°$). The phenyl and pyrrole rings are planar within the error of their determination.

Figure 2 shows the intramolecular bond distances and angles. The standard deviations in bond lengths and angles involving only carbon and nitrogen atoms are of the order of 0.005–0.010 Å. and 0.5–0.8°, respectively. Those for bonds to hydrogen atoms are ~0.05 Å. The accuracy is best for the porphine nucleus and poorest for (C₆H₅)$_\beta$. Of significance are (1) single bonds isolating the phenyl rings from the nucleus; (2) approximate double bonds C-1–C-2 and C-3–C-4, which apparently remove these atoms from the interior resonant system; and (3) flat bonding about the interior carbon atoms.