TABLE III

ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA FOR S_2F_2

	$S^{32}S^{32}F_2$	$S^{32}S^{34}F_2$	$S^{34}S^{32}F_2$
A	8179.12 ± 0.1 Mc.	8118.30 ± 0.2 Mc.	8173.15 ± 0.2 Mc.
B	3968.15 ± .1 Mc.	3950.24 ± .1 Mc.	3834.50 ± .1 Mc.
C	3033.16 ± .1 Mc.	3030.90 ± .4 Mc.	2955.48 ± .4 Mc.
I_A	61.8075 ± 0.0010 Amu. $Å.^2$	62.2705 ± 0.0016 Amu. $Å.^2$	61.8527 ± 0.0016 Amu. $Å.^2$
I_B	127.3971 ± .0030	127.9748 ± .0030	131.8375 ± .0030
I_C	166.6681 ± .0055	166.7989 ± .0300	171.0556 ± .0300
$I_A + I_C - I_B$	101.0785 ± .0095	101.0946 ± .0346	101.0708 ± .0346

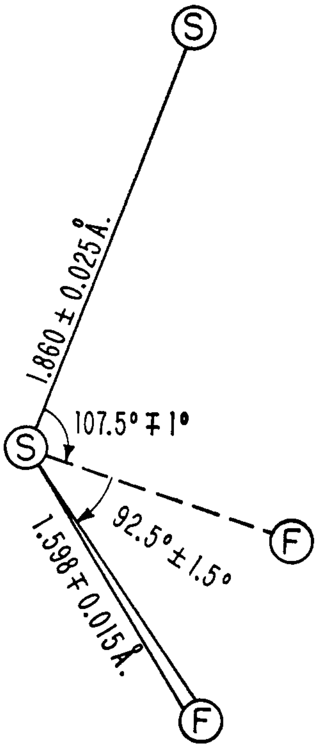

Fig. 1.—Structure of S_2F_2.

(3) The microwave data alone and the moments of inertia obtained therefrom are only reasonable for S_2F_2, for from these data one can show that the molecule contains at least two non-equivalent atoms of sulfur, that it does not contain any other elements which have two or more isotopic species in appreciable abundance, that it is non-planar and therefore has more than three atoms, that the two sulfur atoms lie in a plane of symmetry so that there is at least one equivalent pair of other atoms out of this plane, and finally that the molecule is almost certainly S_2F_2 because other choices lead to interatomic parameters which would conflict either with known ranges of non-bonded distances or known ranges of bonded distances.

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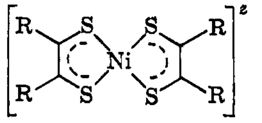
E.s.r. Studies of Four-Coördinate Complexes of Nickel, Palladium and Platinum Related by Electron Transfer Reactions

Sir:

The peculiar diamagnetic nickel complex **1** (R = C_6H_5, z = 0) reported by Schrauzer and Mayweg,[1] and considered by them to be planar, bears a definite relation to the anionic complexes of bivalent metals[2-4] with the dimercaptomaleonitrile anion, $(NC)_2C_2S_2^{-2}$.[2,5] Specifically, the diamagnetic nickel complex **2** (R = CN, z = −2) has two more electrons associated with the metal and the chelate rings than does **1**. Herein we report a novel series of electron transfer reactions, effected both chemically and electrochemically, whereby we have obtained certain of the corresponding members (same z-values) of three series of complexes with R = C_6H_5, CN, CF_3.



M = Ni, Pd, Pt

Treatment of **1** in dimethylsulfoxide (DMSO) solution with p-phenylenediamine produces the anion **3** (R = C_6H_5, z = −1), which gives a strong electron spin resonance signal in DMSO solution with $\langle g \rangle = 2.0568 \pm 0.0003$. The anion can be isolated as the paramagnetic $(C_6H_5)_4As^+$ (1.86 B.M.) and Et_4N^+ (1.82 B.M.) salts.[6] The latter salt in DMSO solution has μ_{eff} = 1.80 B.M. The reduction reaction is readily reversed by I_2 in CH_2Cl_2 solution. Enrichment of **3** in Ni^{61} ($I = 3/2$) indicates the odd electron is localized at least partially on the metal by virtue of the observable electron-nucleus hyperfine splitting, $|a| = 4.5 \pm 1$ gauss. Reaction of **2** or of the corresponding palladium (**4**) and platinum (**5**) complexes (R = CN, z = −2) with I_2 in DMSO solution followed by rapid dilution with an ethanolic solution of tetraethylammonium bromide produced the nickel (**6**) or the palladium (**7**) and platinum (**8**) complexes as black crystalline air-stable 1:1 salts. The moment of solid **6** was found to be ~1.0 B.M. at room temperature, indicating significant exchange demagnetization; however, in acetone solution μ_{eff} = 1.83 B.M., in reasonable agreement with the observed $\langle g \rangle = 2.0633 \pm 0.0004$. This compound represents the first recognized example of a four-coördinate complex containing nickel in a doublet state.[7] Complex **7** is a diamagnetic solid and **8** is a weakly paramagnetic solid (~1.1 B.M.) at room temperature. In 50% v./v. chloroform–dimethylformamide solutions these complexes give intense e.s.r. signals with $\langle g \rangle = 2.0238 \pm 0.0002$ (**7**) and 2.042 ± 0.001 (**8**).[8] In both complexes the hyperfine splitting from the naturally occurring magnetic metal isotopes

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[1] G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

[2] G. Bähr and G. Schleitzer, *Ber.*, **90**, 438 (1957).

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

[4] E. Billig, R. Williams, I. Bernal and H. B. Gray, *Inorg. Chem.*, in press.

[5] H. E. Simmons, D. C. Blomstron and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962).

[6] All compounds referred to herein gave highly satisfactory analyses for carbon and hydrogen and, where appropriate, nitrogen, sulfur and fluorine.

[7] Another example may be the complex formulated as $K_3Ni(CN)_4$ and reported to have a moment of 1.73 B.M.; *cf.* R. Nast and T. von Krakkay, *Z. Naturforsch.*, **9b**, 798 (1954).

[8] Relatively low solubility and slow reaction have thus far prevented accurate measure of magnetic susceptibilities in solution.

are resolvable and are shown in Fig. 1. In **7** (22.2% Pd^{105}, $I = 5/2$) and **8** (33.7% Pt^{195}, $I = 1/2$) $|a| = 7.7 \pm 0.3$ and 82 ± 7 gauss, respectively. These results afford the initial observation of electron-nucleus hyperfine splittings by these nuclei and represent the first characterization of *paramagnetic* four-coördinate complexes of palladium and platinum.

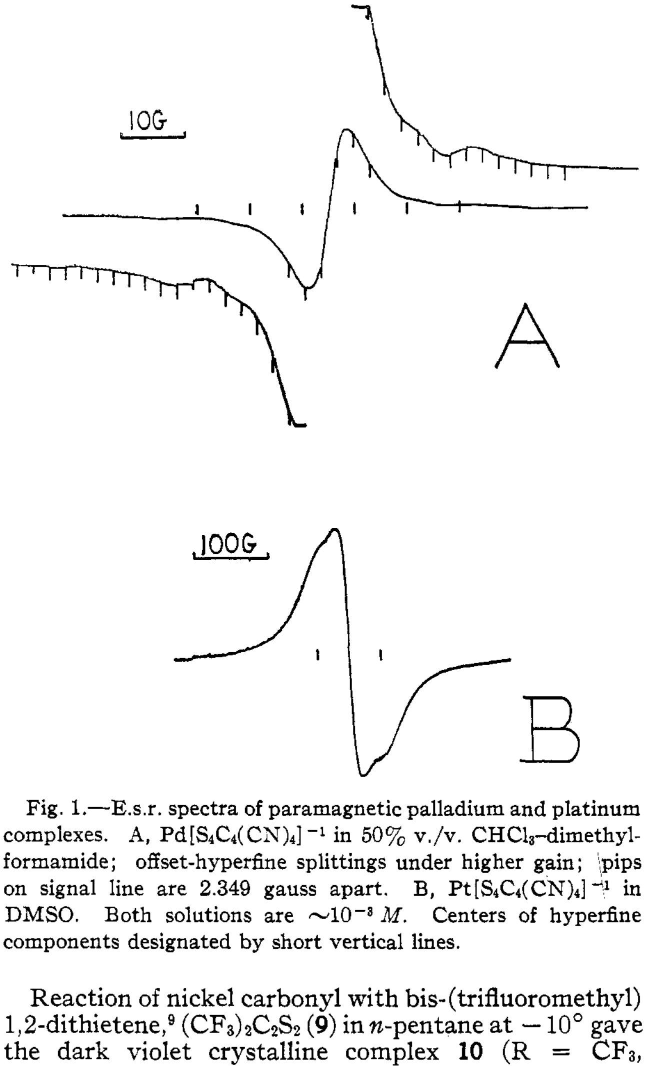

Fig. 1.—E.s.r. spectra of paramagnetic palladium and platinum complexes. A, $\mathrm{Pd[S_4C_4(CN)_4]^{-1}}$ in 50% v./v. $\mathrm{CHCl_3}$–dimethylformamide; offset-hyperfine splittings under higher gain; pips on signal line are 2.349 gauss apart. B, $\mathrm{Pt[S_4C_4(CN)_4]^{-1}}$ in DMSO. Both solutions are $\sim 10^{-3}$ *M*. Centers of hyperfine components designated by short vertical lines.

Reaction of nickel carbonyl with bis-(trifluoromethyl) 1,2-dithietene,[9] $\mathrm{(CF_3)_2C_2S_2}$ (**9**) in *n*-pentane at −10° gave the dark violet crystalline complex **10** ($R = CF_3$, $z = 0$) in nearly quantitative yield. This compound, monomeric in solution and diamagnetic, readily abstracts electrons from basic solvents. Dissolution in dry acetone gives the anion **11** ($R = CF_3$, $z = -1$), which can be precipitated as the dark brown 1:1 tetraethylammonium salt. In acetone solution **11** exhibits the now characteristic e.s.r. spectrum with $\langle g \rangle = 2.0618 \pm 0.0004$. Further reduction by *p*-phenylenediamine in DMSO followed by dilution with an ethanolic solution of $\mathrm{Et_4NBr}$ afforded the yellow diamagnetic 2:1 salt of the anion **12** ($z = -2$).

Polarographic studies in acetonitrile solution demonstrate that **1** undergoes unusually facile reversible one-electron reduction ($E_{1/2} = +0.22$ v.) to **3** while **2, 4** and **5** readily undergo one-electron oxidations at a platinum microelectrode ($E_{1/2} = +0.24, +0.46, +0.26$ v.[10]) to the corresponding anions **6, 7** and **8.** Generation of these uni-negative species in the microwave cavity by controlled potential electrolysis[11] in acetonitrile solution affords e.s.r. spectra identical with those obtained from the chemically synthesized compounds.

Examination of the resonance spectra of the uninegative anions in glass media at ∼100°K. shows in all cases three well separated principal *g*-values, demonstrating marked deviations of the ligand field from axial symmetry. These results are to be contrasted with those obtained from glasses of typical square planar d^9 Cu(II) complexes in which *g*-value anisotropy in the molecular plane has not been resolved.[12,13] In the series $R = CN$, $z = -1$ the following results were obtained: Ni, $g_1 = 1.996$, $g_2 = 2.043$, $g_3 = 2.140$; Pd, $g_1 = 1.956$, $g_2 = 2.046$, $g_3 = 2.065$; Pt, $g_1 = 1.825$, $g_2 = 2.067$, $g_3 = 2.221$.

Full details of synthetic studies of these complexes and others obtained from **9** and of their magnetic and spectral properties will be reported subsequently.

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[9] C. G. Krespan, *J. Am. Chem. Soc.*, **83**, 3434 (1961).

[10] All potentials are relative to s.c.e. and were obtained in purified acetonitrile solution containing 10^{-3} *M* complex and 0.05 *M* $n\text{-}\mathrm{Pr_4NClO_4}$.

[11] D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

[12] See, for example, R. Pettersson and T. Vängård, *Arkiv Kemi*, **17**, 249 (1961); D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961); H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962).

[13] In the related complex $\mathrm{[CuS_4C_4(CN)_4]^{-2}}$, only two *g*-values are obtained in a methanol glass; $g_{\|} = 2.0820$, $g_{\perp} = 2.0238$ (H. B. Gray, I. Bernal and E. Billig, to be published). We thank these authors for permission to quote their results in advance of publication.

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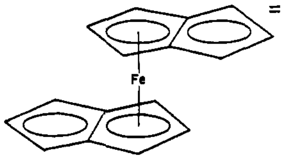
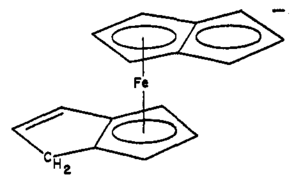
Ferrocene Derivatives of Pentalene: Dipentalenyliron Dianion and Hydrodipentalenyliron Anion

Sir:

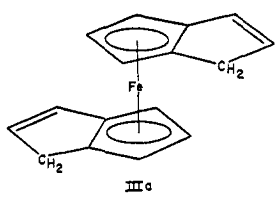
The relationship between the pentalenyl dianion[1] and the cyclopentadienyl anion suggests that the pentalene skeleton might be incorporated into a ferrocene-like molecule. The preparation of the dipentalenyliron dianion (I) and the hydrodipentalenyliron anion (II) is described in this report.



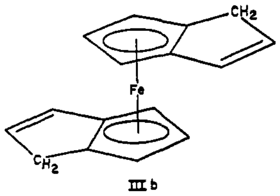
I



II



IIIa



IIIb

Treatment of dihydropentalene in tetrahydrofuran solution with 1.1 mole equivalents of *n*-butyllithium in *n*-hexane and then with ferrous chloride furnishes in 54% yield, after aqueous work-up, sublimation (80°(3 μ)), and crystallization from *n*-hexane, red needles of dihydrodipentalenyliron (III). [M.p. 95–99°; *Anal.* Calcd. for $\mathrm{C_{16}H_{14}Fe}$: C, 73.30; H, 5.38; Fe, 21.32. Found: C, 73.38, 73.04; H, 5.68; 5.40; Fe, 21.29. $\lambda\lambda_{\max}^{\mathrm{EtOH}}$ 282 mμ (ε 7500), 222 mμ (ε 18700).] The bands

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[1] T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).