

TABLE III
ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA FOR S₂F₂

	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

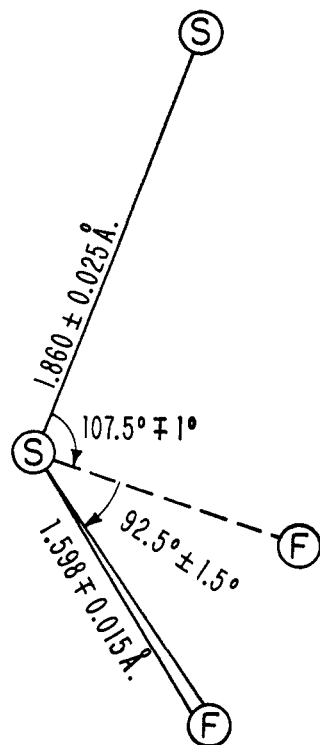


Fig. 1.—Structure of S₂F₂.

(3) The microwave data alone and the moments of inertia obtained therefrom are only reasonable for S₂F₂, 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 S₂F₂ 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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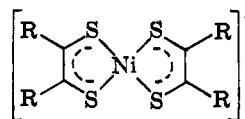
RECEIVED MAY 27, 1963

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 = C₆H₅, z = 0) reported by Schrauzer and Mayweg,¹ and considered by them to be planar, bears a definite rela-

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



M = Ni, Pd, Pt

tion to the anionic complexes of bivalent metals²⁻⁴ with the dimercaptomaleonitrile anion, (NC)₂C₂S₂²⁻.^{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 = C₆H₅, CN, CF₃.

Treatment of 1 in dimethylsulfoxide (DMSO) solution with *p*-phenylenediamine produces the anion 3 (R = C₆H₅, 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 (C₆H₅)₄As⁺ (1.86 B.M.) and Et₄N⁺ (1.82 B.M.) salts.⁶ The latter salt in DMSO solution has $\mu_{\text{eff}} = 1.80$ B.M. The reduction reaction is readily reversed by I₂ in CH₂Cl₂ solution. Enrichment of 3 in Ni⁶¹ ($I = 3/2$) 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 I₂ 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 $\mu_{\text{eff}} = 1.83$ 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

(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. Blomstrom 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 K₂Ni(CN)₄ and reported to have a moment of 1.73 B.M.; cf. R. Nast and T. von Krakay, *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% Pd¹⁰⁵, $I = 5/2$) and **8** (33.7% Pt¹⁹⁵, $I = 1/2$) $|a| = 7.7 \pm 0.3$ 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-coordinate complexes of palladium and platinum.

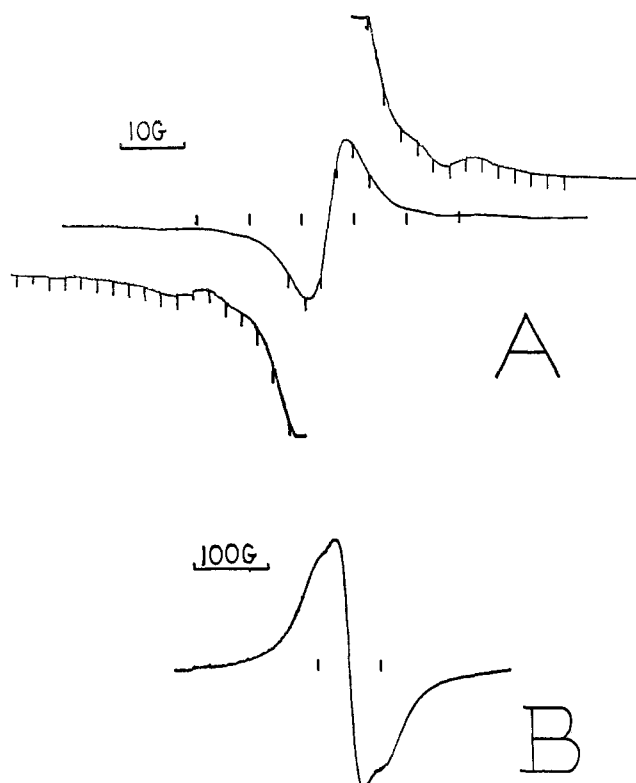


Fig. 1.—E.s.r. spectra of paramagnetic palladium and platinum complexes. A, Pd[S₄C₄(CN)₄]⁻¹ in 50% v/v. CHCl₃-dimethylformamide; offset-hyperfine splittings under higher gain; pips on signal line are 2.349 gauss apart. B, Pt[S₄C₄(CN)₄]⁻¹ in DMSO. Both solutions are $\sim 10^{-3}$ M. Centers of hyperfine components designated by short vertical lines.

Reaction of nickel carbonyl with bis-(trifluoromethyl) 1,2-dithietene,⁹ (CF₃)₂C₂S₂ (**9**) in *n*-pentane at -10° gave the dark violet crystalline complex **10** (R = CF₃, $z = 0$) 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 = CF₃, $z = -1$), 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 Et₄NBr 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 electrolysis¹¹ in acetonitrile solution affords e.s.r. spectra identical with

(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^{-1} M complex and 0.05 M *n*-Pr₄NClO₄.

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

those obtained from the chemically synthesized compounds.

Examination of the resonance spectra of the uni-negative anions in glass media at $\sim 100^\circ$ 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 d⁹ 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.

Acknowledgment.—Financial support by the National Institutes of Health, National Science Foundation, and the Advanced Research Projects Agency (Contract SD-88) is gratefully acknowledged.

(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 [CuS₄C₄(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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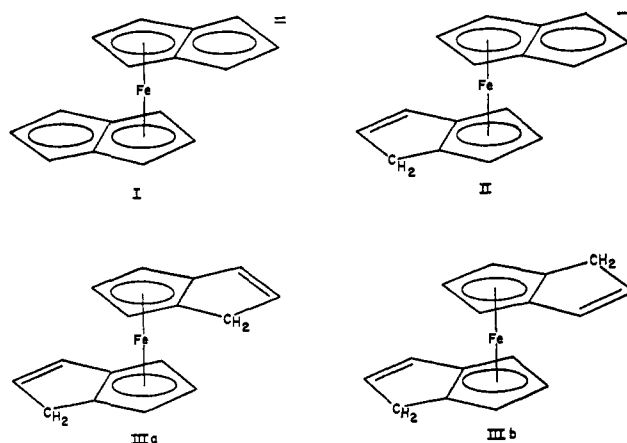
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RECEIVED APRIL 23, 1963

Ferrocene Derivatives of Pentalene: Dipentalenylyliron Dianion and Hydrodipentalenylyliron Anion

Sir:

The relationship between the pentalenyl dianion¹ and the cyclopentadienyl anion suggests that the pentalene skeleton might be incorporated into a ferrocene-like molecule. The preparation of the dipentalenylyliron dianion (I) and the hydrodipentalenylyliron anion (II) is described in this report.



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 dihydrodipentalenylyliron (III). [M.p. $95-99^\circ$; *Anal.* Calcd. for C₁₆H₁₄Fe: C, 73.30; H, 5.38; Fe, 21.32. Found: C, 73.38, 73.04; H, 5.68; 5.40; Fe, 21.29. $\lambda_{\text{max}}^{\text{EtOH}}$ 282 μm (ϵ 7500), 222 μm (ϵ 18700).] The bands

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