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The Preparation and Characterization of Four-Coordinate Complexes Related by Electron-Transfer Reactions

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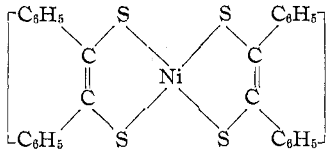
The synthesis and characterization of a new series of four-coordinate complexes of the general type $[MS_4C_4R_4]^z$ are described in detail. Three series of complexes have been obtained. With R = C_6H_5 and CF_3 and M = Ni three species have been obtained with $z = 0, -1$, and -2. With R = CN a series of new mononegative anionic complexes was prepared containing M = Cu, Co, Ni, Pd, Pt, and Au. The related species with $z = -2$ have been previously reported.[2,3] All known numbers of these three series are readily interconverted by electron-transfer reactions. Polarographic half-wave potentials for the oxidation–reduction couples are tabulated. The mononegative anions of Ni, Pd, and Pt contain the metal in the doublet spin state and have been examined by electron spin resonance. The initial observations of hyperfine splittings by Ni^{61}, Pd^{105}, and Pt^{195} are reported. The presence of three principal *g*-values in the glass spectra of the complexes demonstrates the marked deviations of the ligand fields in these complexes from axial symmetry.

Introduction

Two very recent independent reports of syntheses and properties of four-coordinate complexes of nickel and other transition elements with certain bidentate ligands furnishing sulfur as the donor atom imply the existence of a heretofore unrecognized series of complexes differing only in the total number of valence electrons. The first pertinent result is that of Schrauzer and Mayweg,[1] who obtained the neutral complex **1** by reaction of nickel sulfide with diphenylacetylene or by reaction of nickel carbonyl, sulfur, and diphenylacetylene. Shortly thereafter, Gray, *et al.*,[2,3] reported the characterization of a number of bis complexes derived from the dinegative *cis*-1,2-dicyanoethylene-1,2-dithiolate anion,[4,5] including the diamagnetic nickel complex anion **2**.



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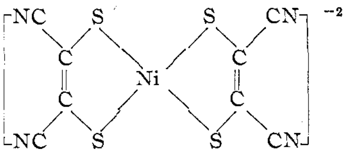

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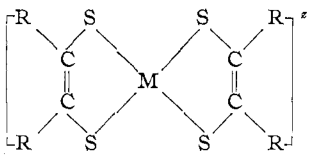
Inspection of **1** and **2** reveals a difference of two electrons associated with the central metal and the two chelate rings, the substituents being excluded. The easy isolation and characterization of **1** and **2** suggests reasonable stabilities associated with both electronic arrangements and raises the possibility that **1** and related species might be reducible to mono- and/or dinegative anions, whereas **2** and related species might be oxidizable to a mononegative anion and/or a neutral complex. We have investigated the synthesis of complexes of the general type **3** by electron-transfer reactions and in this way have obtained certain of the corresponding members of three series of complexes with R = CN, CF_3, C_6H_5. These studies have yielded the first well-authenticated example of a four-coordinate complex containing nickel in a doublet state and the first four-coordinate *paramagnetic* complexes of palladium and platinum of any description. Herein we report the details of the preparations of these series of complexes, a summary of the chemical properties, and those results of magnetic susceptibility, conductivity, electron spin resonance, and optical spectral studies which serve to characterize the members of this series. Full discussion of the optical spectra and electron resonance will be presented in a subsequent communication. Certain preliminary results have already been reported.[6]



R = CN, CF_3, C_6H_5
z = 0, −1, −2

3

Experimental

Preparation of Compounds.—Disodium *cis*-1,2-dicyanoethylene 1,2-dithiolate was prepared according to Bähr and Schleitzer[4] and used after one recrystallization from ethanol–ether. Salts of the dinegative complex anions of this ligand containing nickel, copper, cobalt, palladium, and platinum were prepared in a manner similar to that of Billig, *et al.*[3]

All melting points are uncorrected.

$[NiS_4C_4(C_6H_5)_4]$.—This complex was prepared by the methods indicated.[1] It was found possible to obtain yields of only 2–3.5% based on nickel starting material. The product was recrystallized from toluene to give greenish black needles.

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

[2] H. B. Gray, R. Williams, I. Bernal, and E. Billig, *ibid.*, **84**, 3596 (1962).

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

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

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

[6] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 2029 (1963).

Anal. Calcd.: C, 61.89; H, 3.71; S, 23.60. Found: C, 61.84; H, 3.68; S, 23.44.

$[(C_2H_5)_4N][NiS_4C_4(C_6H_5)_4]$.—$NiS_4C_4(C_6H_5)_4$ (0.57 g.) and pure *p*-phenylenediamine (0.3 g.) were dissolved in 2 ml. of freshly distilled oxygen-free dimethyl sulfoxide (DMSO) under nitrogen. An intense red-brown color developed immediately. This solution was poured into a solution of 0.5 g. of tetraethylammonium bromide in 50 ml. of ethanol. Red platelets crystallized rapidly from the solution. This product was recrystallized from a hot solution of acetone (10 ml.) and methanol (25 ml.). The shiny purple-red platelets thus obtained were washed with cold methanol (5 ml.) and dried *in vacuo;* m.p. 290° dec.

Anal. Calcd.: C, 64.19; H, 5.99; S, 19.04; N, 2.12. Found: C, 64.08; H, 5.95; S, 19.26; N, 2.12.

The anion in methylene chloride solution can be oxidized quantitatively to the parent neutral complex by treatment with a stoichiometric amount of iodine.

$[(C_6H_5)_4As][NiS_4C_4(C_6H_5)_4]$.—This compound was obtained by the above procedure using tetraphenylarsonium chloride in methanol as a precipitant. The product crystallized slowly from the resulting solution cooled in ice–salt mixture. Recrystallization from acetone–methanol (1:9 v./v.) gave purple crystals, which were washed with methanol and dried *in vacuo;* m.p. 254–256° dec.

Anal. Calcd.: C, 67.39; H, 4.35; S, 13.84. Found: C, 66.80; H, 4.35; S, 13.99.

$[NiS_4C_4(CF_3)_4]$.—$Ni(CO)_4$ (3 ml.) dissolved in 100 ml. of *n*-pentane was added in one portion to a cold (−10 to 0°) solution of 10.5 g. of bis-perfluoromethyl-1,2-dithiete[7] in 200 ml. of *n*-pentane. An intense blue-violet color developed within 15 sec. and within 1–2 min. vigorous evolution of CO gas occurred. After the termination of observable gas evolution the solution was allowed to stand at 0° for 1–2 hr. to ensure complete reaction. The solvent was removed, leaving 11.8 g. (98%) of crude product as purple-black needle-like crystals. Recrystallization from benzene or *n*-pentane afforded shiny black crystals, m.p. 134–135° (sealed tube). The crude product may also be purified by sublimation at 120° (0.01 mm.).

Anal. Calcd.: C, 18.80; S, 25.10; F, 44.62; Ni, 11.49. Found: C, 18.83; S, 24.95; F, 44.38; Ni, 11.7.

$[(C_2H_5)_4N][NiS_4C_4(CF_3)_4]$.—$NiS_4C_4(CF_3)_4$ (5 g.) was dissolved in 40 ml. of acetone. The solution color changed rapidly from dark purple to blue to brown-green as the nickel species oxidized the solvent. To this solution was added 2.2 g. of tetraethylammonium bromide in 300 ml. of isopropyl alcohol–water (40% v./v.). The red-brown crystals produced were collected, washed with water, and recrystallized from a mixture of acetone (10 ml.) and isobutyl alcohol (25 ml.) by addition of 200 ml. of *n*-pentane; 3.9 g. (62%) of red-brown platelets separated by filtration and were washed with *n*-pentane and air-dried, m.p. 119–120°.

Anal. Calcd.: C, 29.97; H, 3.14; N, 2.18; S, 20.00; F, 35.55. Found: C, 30.13; H, 3.17; N, 2.22; S, 20.14; F, 36.44.

$[(C_6H_5)_4As][NiS_4C_4(CF_3)_4]$.—This compound was prepared like the tetraethylammonium salt except that DMSO was used as the reduction medium. The product was recrystallized from a hot mixture of isopropyl alcohol (25% v./v.), isobutyl alcohol (25% v./v.), and ethanol (50% v./v.). Slow cooling produced long well-formed red-black crystals which were washed with isobutyl alcohol and *n*-pentane and air-dried; m.p. 174–174.5°.

Anal. Calcd.: C, 42.98; H, 2.25; S, 14.34; F, 25.49. Found: C, 42.97; H, 2.38; S, 14.44; F, 25.33.

$[(C_2H_5)_4N]_2[NiS_4C_4(CF_3)_4]$.—A solution of 2.05 g. of the 1:1 tetraethylammonium salt in 10 ml. of DMSO was treated with 0.8 g. of *p*-phenylenediamine. The initially brown-green solution became extremely dark brown, whereupon 1.6 g. of tetraethylammonium bromide in 100 ml. of ethanol was added. The color of the solution changed to dark green and on cooling to 0° golden yellow crystals were slowly deposited. These were collected, washed with cold absolute ethanol until the washings were pale yellow in color, and finally washed with *n*-pentane. The product (1.95 g., 79%) was recrystallized from acetone–ethanol to give golden yellow crystals, m.p. 248–251° dec.

Anal. Calcd.: C, 37.36; H, 5.23; S, 16.62; N, 3.63; F, 29.55. Found: C, 37.79; H, 5.31; S, 16.78; N, 3.84; F, 29.40.

$[(C_2H_5)_4N][NiS_4C_4(CN)_4]$.—Iodine (4.5 g.) in 5 ml. of freshly distilled DMSO was added quickly in one portion to 9.0 g. of $[(C_2H_5)_4N]_2[NiS_4C_4(CN)_4]$ in 10 ml. of DMSO. On mixing the solution turned from red to very dark brown. Immediate addition of 130 ml. of ethanol caused rapid crystallization of the product (5.8 g., 83%) as fine black needles, which, after washing with ethanol and ether, is pure enough for most purposes. Further purification can be effected by recrystallization from acetone; m.p. 288–290°.

Anal. Calcd.: C, 40.95; H, 4.30; S, 27.33; N, 14.92. Found: C, 41.23; H, 4.56; S, 27.52; N, 14.87.

$[(n\text{-}C_4H_9)_4N][NiS_4C_4(CN)_4]$.—This compound was prepared from the tetrabutylammonium 2:1 nickel complex by the above procedure; m.p. 171–172°.

Anal. Calcd.: C, 49.57; H, 6.24; N, 12.04. Found: C, 49.93; H, 6.32; N, 11.95.

$[(C_5H_5)_2Co][NiS_4C_4(CN)_4]\cdot 2CH_3COCH_3$.—To a filtered solution of 2.65 g. of $[(C_2H_5)_4N][NiS_4C_4(CN)_4]$ in 90 ml. of acetone was added a solution of anhydrous cobalticinium chloride in acetone–ethanol (90/10 v./v.). The shiny black crystals which immediately precipitated were collected, washed with ethanol and ether, and air-dried. The product slowly lost weight upon heating (150°, 0.01 mm.) but only 70% of the acetone was removed after 2 days; an intense infrared band at 1710 $cm.^{-1}$ was observed in dichloromethane solution.

Anal. Calcd.: C, 44.74; H, 3.44; N, 8.72. Found: C, 45.10; H, 2.70; N, 8.82.

$[R_4N][PdS_4C_4(CN)_4]$. (a) **By Iodine Oxidation.**—This preparation is exactly analogous to that for the nickel complex except that a large excess of iodine is required. $[(C_2H_5)_4N]_2[PdS_4C_4(CN)_4]$ (3.4 g.) in 20 ml. of DMSO was treated with 6.4 g. of iodine in 10 ml. of DMSO. Immediate addition of 150 ml. of ethanol gave black crystals which were washed with ethanol and ether and dried *in vacuo* at 80°; 1.8 g., 66%, m.p. 275° dec.

Anal. Calcd.: C, 37.17; H, 3.90; S, 24.80; N, 13.55. Found: C, 37.46; H, 3.91; S, 25.57; N, 13.37.

(b) **By Oxidation with $NiS_4C_4(CF_3)_4$.**—$[(n\text{-}C_4H_9)_4N]_2[PdS_4C_4(CN)_4]$ (1.0 g.) was dissolved in 90 ml. of hot dichloromethane. To this solution was added 0.59 g. of the nickel complex. A color change from green to red-brown occurred. Reduction of the volume to ~15 ml. and cooling produced black crystals which were washed with 2 ml. of cold dichloromethane. Recrystallization from dichloromethane gave 0.43 g. (61%) of black crystals; m.p. 190–191°.

Anal. Calcd.: C, 45.81; H, 5.77; N, 11.13. Found: C, 46.11; H, 5.79; N, 10.91.

$[(C_2H_5)_4N][PtS_4C_4(CN)_4]$.—This compound was prepared as black crystals in 73% yield by iodine oxidation of $[(C_2H_5)_4N]_2[PtS_4C_4(CN)_4]$ in a manner analogous to that for the nickel complex. The product was not recrystallized; m.p. 288° dec.

Anal. Calcd.: C, 31.73; H, 3.33; S, 21.17; N, 11.56. Found; C, 31.81; H, 3.37; S, 21.66; N, 11.33.

$[(C_2H_5)_4N][AuS_4C_4(CN)_4]$.—One equivalent of $HAuCl_4\cdot 3H_2O$ in aqueous solution was neutralized to pH 6–7 and added with stirring to an aqueous solution of two equivalents of $Na_2S_2C_2(CN)_2$. Addition of tetraethylammonium bromide precipitated the product, which was then recrystallized twice from 1:2 acetone–*n*-propyl alcohol to yield lustrous red-brown needles.

Anal. Calcd.: C, 31.63; H, 3.32; N, 11.53. Found: C, 31.75; H, 3.34; N, 11.76.

$[(C_4H_9)_4N][CoS_4C_4(CN)_4]$.—$[(n\text{-}C_4H_9)_4N]_2[CoS_4C_4(CN)_4]$ (3.23 g.) in 60 ml. of hot dichloromethane was treated with 2.05 g. of $NiS_4C_4(CF_3)_4$, after which the solution changed from red-brown to greenish brown. Cooling produced black crystals which were filtered, washed with ethanol, and air-dried to yield 1.6 g. (76%); m.p. 198–199°.

Anal. Calcd.: C, 49.55; H, 6.24; S, 22.04; N, 12.04. Found: C, 49.25; H, 6.16; S, 22.11; N, 11.67.

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(7) C. G. Krespan, *J. Am. Chem Soc.*, **83**, 3434 (1961).

TABLE I

CONDUCTIVITY AND MAGNETIC SUSCEPTIBILITY DATA[a]

		Solid		Solution		
	Λ^c	$10^6\chi^M_{cor}$	μ_{eff}, B.M.[b]	$10^6\chi^M_{cor}$	Solvent	μ_{off}, B.M.[b]
$[NiS_4C_4(C_6H_5)_4]$	. . .	60	~0	. . .	. . .	. . .
$[(C_2H_5)_4N][NiS_4C_4(C_6H_5)_4]$	68	1397	1.82	1361	DMSO	1.80
$[(C_6H_5)_4As][NiS_4C_4(C_6H_5)_4]$	52	1454	1.86	. . .	. . .	. . .
$[(C_6H_5)_4As]_2[NiS_4C_4(C_6H_5)_4]$	. . .	Dia.[e]	0	. . .	. . .	. . .
$[NiS_4C_4(CF_3)_4]$	. . .	Dia.[e]	0	Dia.	C_6H_{12}	0[f]
$[(C_2H_5)_4N][NiS_4C_4(CF_3)_4]$	81	1438	1.85	1479	Acetone	1.88[g]
$[(C_6H_5)_4As][NiS_4C_4(CF_3)_4]$	64	1398	1.82	. . .	. . .	. . .
$[(C_4H_9)_4N][NiS_4C_4(CF_3)_4]$	70	. . .	. . .	. . .	. . .	. . .
$[(C_2H_5)_4N]_2[NiS_4C_4(CF_3)_4]$	148	Dia.[e]	0	. . .	. . .	. . .
$[(C_2H_5)_4N][NiS_4C_4(CN)_4]$	81	438	1.02	1404	Acetone	1.83
$[(C_4H_9)_4N][NiS_4C_4(CN)_4]$	69	1002	1.54	. . .	. . .	. . .
$[(C_5H_5)_2Co][NiS_4C_4(CN)_4]$	. . .	766	1.35	. . .	. . .	. . .
$[(C_2H_5)_4N][PdS_4C_4(CN)_4]$[d]	83	Dia.[e]	0	. . .	. . .	. . .
$[(C_4H_9)_4N][PdS_4C_4(CN)_4]$[d]	68	Dia.[e]	0	. . .	. . .	. . .
$[(C_2H_5)_4N][PtS_4C_4(CN)_4]$	81	464	1.05	1361	Acetone	1.80
$[(C_4H_9)_4N][CoS_4C_4(CN)_4]$	74	Dia.[e]	0	. . .	. . .	. . .
$[(C_4H_9)_4N][CuS_4C_4(CN)_4]$	69	Dia.[e]	0	. . .	. . .	. . .
$[(C_2H_5)_4N][AuS_4C_4(CN)_4]$	80	Dia.[e]	0	. . .	. . .	. . .

[a] Obtained at 22–25°. [b] Calculated from Curie law, $\mu_{eff} = 2.84(\chi^m_{cor}T)^{1/2}$. [c] Cm.^{2} equiv.$^{-1}$ ohm^{-1} in nitromethane solution. [d] Decomposes very rapidly in polar solvents. [e] Accurate susceptibility not determined. [f] Also diamagnetic in chloroform, n-pentane, methylene chloride solution. [g] 1.88 B.M. in DMSO solution.

$[(C_4H_9)_4N][NiS_4C_4(CF_3)_4]$.—The filtrate from the preceding reaction was evaporated to dryness, the solid residue was treated with hot 80% aqueous ethanol, and the hot solution was filtered to remove the residual cobalt complex. Cooling of the solution afforded long green-brown needles which were separated and recrystallized from 80% aqueous ethanol; m.p. 107.5–109°.

Anal. Calcd.: C, 38.25; H, 4.82; S, 17.02; N, 1.86. Found: C, 38.69; H, 5.04; S, 16.84; N, 2.17.

$[(C_4H_9)_4N][CuS_4C_4(CN)_4]$.—Oxidation of $[(n\text{-}C_4H_9)_4N]_2[CuS_4C_4(CN)_4]$ with $NiS_4C_4(CF_3)_4$ in a manner analogous to that for the palladium and cobalt complexes yielded after one recrystallization from 1:1 ethanol–dichloromethane dark red needles; m.p. 146.5–147°.

Anal. Calcd.: C, 49.16; H, 6.19; N, 11.95. Found: C, 49.21; H, 6.17; N, 11.96.

Magnetic Measurements.—Magnetic susceptibilities were measured by the Gouy method using distilled water and aqueous nickel chloride solutions as standards.

Electron Spin Resonance Measurements.—Measurements were made on an e.s.r. spectrometer which is a slightly modified version of the one described previously.[8] It now employs a 175 kc./sec. magnetic field modulation. The klystron frequency is measured by a Hewlett-Packard transfer oscillator in conjunction with a Hewlett-Packard frequency counter. The same frequency counter is used with the proton resonance spectrometer which monitors the magnetic field. The proton probe is placed along the same axis of the magnetic field as is the sample in the cavity.

Polarographic Measurements.—Half-wave potentials were obtained on an automatic recording Leeds & Northrup Type E Electrochemograph. Potentials were measured at room temperature relative to an aqueous calomel electrode saturated with NaCl. A rotating platinum microelectrode was used as the indicator electrode. All solutions were 0.05 M in $[(n\text{-}C_3H_7)_4N](ClO_4)$ as the supporting electrolyte, $\sim 10^{-3}$ M in complex, and were prepared from freshly purified dimethyl sulfoxide or spectro grade acetonitrile.

Conductivity Measurements.—Conductivities were measured on a Serfass conductivity bridge using $\sim 10^{-3}$ M solutions prepared from spectro grade nitromethane.

Results and Discussion

All of the compounds synthesized in this work are set out in Table I. With the exception of 1, bis-(*cis*-1,2-diphenylethylene-1,2-dithiolato)-nickel, none of these compounds has been prepared previously. The cumulative evidence from elemental analyses, conductivities, and magnetic moments establishes the composition of these compounds. Comparison of conductivities in nitromethane solution with literature values[3,9] shows that all salts behave as uni-univalent or biunivalent electrolytes, in agreement with their formulation.

The polarographic and e.s.r. results are presented in Tables II and III. The electron-transfer reactions discussed below are readily understood by reference to the polarographic half-wave potentials of the oxidizing couples.

The structure of none of the compounds is known with certainty. It has been shown[2,3] that the complex salts $[(C_4H_9)_4N]_2[MS_4C_4(CN)_4]$ (M = Ni, Co, Pd, or Pt) are isomorphous and so isostructural, and presumably planar. Among the compounds prepared in this work, powder patterns[10] of $(R_4N)[MS_4C_4(CN)_4]$ revealed isomorphism in the groups R = n-C_4H_9, M = Cu, Ni, or Co, and R = C_2H_5, M = Au or Pt. Because the copper and gold monoanions are diamagnetic and contain metals which are formally d^8, there seems little doubt that these complexes and those isomorphous with them are essentially or exactly planar. There are no known cases of four-coordinate diamagnetic d^8 complexes which do not have these structures.

Chemical Results. (a) **R = C_6H_5 Series.**—We have confirmed completely the reported synthesis of 1, which represents the first member of the series. In accord with expectation it has proven possible to reduce 1 by addition of one and two electrons to produce the

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(8) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

(9) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(10) Powder data were obtained on a Phillips Norelco X-Ray Diffractometer using Cu Kα radiation (Ni filter). We are indebted to M. C. Babineau of A. D. Little, Inc., Cambridge, Mass., for these results.

TABLE II

POLAROGRAPHIC HALF-WAVE POTENTIALS OF COMPLEXES IN ACETONITRILE SOLUTION

R	Couple	$E^1/_2$, v.[c]
C_6H_5[a]	$(Ni)^{-2} \rightleftharpoons (Ni)^{-} + e^{-}$	−0.74[b]
CF_3	$(Ni)^{-2} \rightleftharpoons (Ni)^{-} + e^{-}$	− .121[b]
CN	$(Co)^{-2} \rightleftharpoons (Co)^{-} + e^{-}$	+ .050
C_6H_5[a]	$(Ni)^{-} \rightleftharpoons (Ni)^{0} + e^{-}$	+ .224[b]
CN	$(Pt)^{-2} \rightleftharpoons (Pt)^{-} + e^{-}$	+ .210
CN	$(Ni)^{-2} \rightleftharpoons (Ni)^{-} + e^{-}$	+ .226
CN	$(Cu)^{-2} \rightleftharpoons (Cu)^{-} + e^{-}$	+ .330
CN	$(Pd)^{-2} \rightleftharpoons (Pd)^{-} + e^{-}$	+ .440
CF_3	$(Ni)^{-} \rightleftharpoons (Ni)^{0} + e^{-}$	+ .997[b]

[a] Measured in DMSO solution. [b] In each case the two waves possess nearly equal diffusion currents. [c] Obtained at ambient room temperature; potentials corrected for *IR* drop in polarographic cell; estimated error ±0.01 v.

TABLE III

$<g>$-VALUES FOR COMPLEXES IN SOLUTION

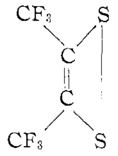
Complex	Solvent	$<g>$
$[NiS_4C_4(C_6H_5)_4]^-$	DMSO	2.0568 ± 0.0003[a]
$[NiS_4C_4(CF_3)_4]^-$	Acetone	$2.0618 \pm .0004$
$[NiS_4C_4(CN)_4]^-$	Acetone	$2.0633 \pm .0004$
$[PdS_4C_4(CN)_4]^-$	$CHCl_3$–DMF[b]	$2.0238 \pm .0002$[a]
$[PtS_4C_4(CN)_4]^-$	$CHCl_3$–DMF[b]	$2.042 \pm .001$[a]

[a] Electron–nucleus hyperfine splittings: Ni^{61} (synthetically enriched, $I = {}^3/_2$), $|a| = 4.5 \pm 1$ gauss; Pd^{105} (22.2%, $I = {}^5/_2$), $|a| = 7.7 \pm 0.3$ gauss; Pt^{195} (33.7%, $I = {}^1/_2$), $|a| = 82 \pm 7$ gauss. [b] 50% v./v.

second and third members of the series. The first half-wave potential indicates the very considerable ease of reduction and, accordingly, it is possible to form the uninegative anion in DMSO solution by use of a wide variety of reducing agents including metallic mercury, copper, aluminum, magnesium, zinc, LiI, and R_4NOH. For synthetic purposes the uninegative ion is readily obtained using *p*-phenylenediamine. In all cases the reduction product is readily characterized by an intense and characteristic e.s.r signal at $\langle g \rangle = 2.057$. In connection with the ease of reduction of **1**, it must be pointed out that Schrauzer and Mayweg[1] claimed that in pyridine and piperidine solution this complex gave magnetic moments of 1.9 and 2.5 B.M.,[11] respectively, and produced red-brown solutions. We have found that solutions of **1** in these solvents are initially green, but slowly turn red-brown and develop the characteristic e.s.r. signal of the uninegative anion, the intensity of which increases with time. We therefore suggest that at least a fraction of the paramagnetism measured arises from this anion, and that the total paramagnetism cannot result from the formation of axial bis-solvates alone as has been supposed.[1]

Comparison of the first half-wave potentials for **1** and for tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethan (TCNQ)[12] reveals that these compounds are π-acids or oxidizing agents of comparable strengths. This is especially evident in view of the ability of **1** and TCNE to oxidize numerous metals at room temperature to give the corresponding metal salts of uninegative anions and to react with iodide ion and aliphatic and aromatic amines.[13,14] In addition, the second reduction half-wave potential of TCNE occurs at −0.561 v.[14] *vs.* −0.74 v. for reduction to $[NiS_4C_4(C_6H_5)_4]^{-2}$. The chemical synthesis of this anion is best effected by reduction of **1** in tetrahydrofuran solution with sodium amalgam. Analytically pure salts were not obtained due to the extreme ease of oxidation of the anion in the solid and in solution to the uninegative anion. However, it was verified that the orange tetraphenylarsonium salt is diamagnetic.

(b) R = CF_3 Series.—Bis-(trifluoromethyl)-1,2-dithiete, **4**, reacts rapidly with nickel carbonyl[15] in



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n-pentane at −10° to give purple-black air-stable crystals of the neutral diamagnetic complex bis-(*cis*-1,2-trifluoromethylethylene-1,2-dithiolato)-nickel, **5** (**3**, R = CF_3, z = 0). This compound is analogous to **1** and represents the first member of this series. It is extremely soluble in nonpolar solvents such as pentane, cyclohexane, benzene, and dichloromethane to give intense purple solutions in which the complex is diamagnetic. In more basic solvents such as ketones, amides, nitriles, amines, and DMSO, **5** reacts readily to form brown-green solutions containing the uninegative anion **6**, detected by its characteristic absorption spectrum and e.s.r. signal ($\langle g \rangle = 2.0618$).[16] These are identical with the results obtained from the chemically prepared species, which is readily produced by reduction in acetone solvent followed by precipitation with a large cation. In mesitylene, a π-base superior to benzene,[17] or in a dilute solution of mesitylene in *n*-pentane, addition of **5** develops an intense blue color and an e.s.r. signal of the monoanion is detectable. In pure mesitylene the solute is weakly paramagnetic with a moment of 0.89 B.M./Ni. From these observations it is evident that **5** is a π-acid of great strength and is considerably stronger than either TCNE or TCNQ as judged from a comparison of half-wave potentials[12] (*cf.* Table II).

The second half-wave potential of **5** is considerably less negative than that of **1** or TCNE and, correspond-

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(11) Attempts to reproduce these measurements were unsatisfactory because of the low solubility (~10^{-2} *M*) in these solvents.

(12) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962); the following values are given (acetonitrile, 0.1 *M* $LiClO_4$): TCNE–$TCNE^{\cdot-}$, +0.152; TCNQ–$TCNQ^{\cdot-}$, +0.127 v.

(13) O. W. Webster, W. Mahler, and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).

(14) O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).

(15) R. B. King (*ibid.*, **85**, 1587 (1963)) allowed these two compounds to react under conditions which did not yield **5**. No identifiable products were reported. We thank Dr. King for a preprint of his work just prior to its publication.

(16) Reduction to the mononegative ion is not the only process occurring in these solutions. In acetone, DMSO, and DMF the paramagnetic susceptibility per nickel (2400×10^{-6}) is far too large to result from the monoanion alone. Chemical tests show the presence of Ni^{+2} and free **4** in these solutions. The course of these reactions is being further investigated.

(17) See, for example, R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

ingly, the uninegative species is easily reduced by a variety of reagents including aromatic amines. The use of *p*-phenylenediamine in DMSO solution gave the yellow-orange dinegative anion which was isolated as the diamagnetic tetraethylammonium salt. This anion can be oxidized to the −1 stage by iodine in dichloromethane. Its solutions are slowly oxidized by air.

The powerful electron acceptor ability of **5** mentioned above, which makes it a better one-electron oxidizing agent than either TCNE or TCNQ, renders it highly useful in effecting certain electron-transfer reactions. In this work we have utilized **5** to perform one-electron oxidations in methylene chloride solution on the species $[MS_4C_4(CN)_4]^{-2}$ according to the reaction

$$NiS_4C_4(CF_3)_4 + [MS_4C_4(CN)_4]^{-2} \longrightarrow [NiS_4C_4(CF_3)_4]^{-1} + [MS_4C_4(CN)_4]^{-1}$$

$$M = Cu, Co, Ni, Pd, Pt$$

Quaternary ammonium salts of the cyano anions are only sparingly soluble in this solvent and are easily separated from the extremely soluble R_4N^+ salts of the trifluoromethyl monoanion.

(c) **R = CN Series.**—The dinegative anions of this series have already been prepared.[2,3] Oxidation of these species with iodine in DMSO solution or with $NiS_4C_4(CF_3)_4$ in dichloromethane solution afforded the Cu, Co, Ni, Pd, and Pt monoanions, which are readily precipitated as crystalline solids. The monoanions of the nickel group are reduced to the dianions by treatment with basic solvents. When prepared in DMSO solution, very rapid dilution with an ethanolic solution containing R_4N^+ so as to effect quick precipitation is essential in order to obtain pure product. The palladium monoanion is especially sensitive to reduction by solvent, as might be expected from the relatively large half-wave potential for the couple $(Pd)^{-2} \rightleftharpoons (Pd)^- + e^-$ (*cf.* Table III). It is appreciably reduced in such weakly basic solvents as acetone and nitromethane over the course of ~15 min. All attempts to recrystallize this complex from basic solvents gave salts of the dianion. However, the tetrabutylammonium salt can be recrystallized from dichloromethane to give an analytically pure product.

The oxidative polarograms of all dianions of this series failed to show a second oxidation wave having approximately the same diffusion current as the first wave. A second ill-defined wave was generally observed at ~+1 v., but the extremely large currents associated with it indicated multi-electron oxidation processes. Hence, the neutral complexes $[MS_4C_4(CN)_4]$, which are the first members of this series, could not be obtained by reactions carried out under strongly oxidizing conditions. Additionally, the parent ligand, dicyano-1,2-dithiete, has as yet not been isolated.[5]

Magnetic Susceptibility and Electron Spin Resonance Results.—Magnetic susceptibilities and moments are given in Table I and average *g*-values for complexes in solution are set out in Table III. The paramagnetic complexes in this work are those obtained by one-electron oxidations of the anions **3**, R = CN, $z = -2$, M = Ni, Pd, or Pt, and one-electron reduction of the complexes **3**, R = C_6H_5 or CF_3, $z = 0$, M = Ni. The resultant complexes are clearly isoelectronic in a valency sense and represent for Ni, Pd, and Pt a new type of paramagnetic species. In solution these paramagnetic ions display intense e.s.r. signals at room temperature. The paramagnetism thus detected is conclusively shown to arise from an $S = 1/2$ ground state in the cases of M = Ni or Pt from measurements of solution magnetic moments. The paramagnetic palladium complex is assumed to be of the same type. Unfortunately, rapid reaction with those solvents in which salts of this anion are sufficiently soluble for susceptibility measurements has thus far prevented an accurate determination of the magnetic moment of this anion in solution.

In the solid state the mononegative nickel complexes of the R = CF_3 and C_6H_5 series show normal moments for one unpaired electron. However, the paramagnetic complexes of the R = CN series show subnormal magnetic moments, indicating considerable exchange demagnetization. Both salts of the palladium complex are diamagnetic. A general increase in cation size increases the susceptibility of the nickel monoanion, an effect undoubtedly due to increasing magnetic dilution.

Only a very few paramagnetic compounds of palladium and platinum of any structural type are known. The monoanions are the only examples of four-coordinate paramagnetic species. The other paramagnetic compounds of these metals are PdF_3[18] and O_2^+-PtF_6^-.[19] The nickel monoanion represents the only known case of a four-coordinate complex containing nickel in the doublet state. The closest approaches to this situation among known compounds are the tetragonal six-coordinate species bis-(*o*-phenylenedimethylarsine)-nickel(III) dibromo and dichloro cations, which have one unpaired electron.[20] No e.s.r. studies of these species have been reported. The compound $K_3Ni(CN)_4$ (μ_{eff} = 1.73 B.M.) has been claimed[21] but its structure is unknown. The only other nickel complex with one unpaired spin is $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$,[22] the electron spin resonance of which has been measured in a single crystal.[23]

Of especial importance in the e.s.r. measurements is the resolvable hyperfine interactions due to Ni^{61}, Pd^{105}, and Pt^{195}. These hyperfine splittings demonstrate that the odd electron is localized at least partially on the metal. The hyperfine interaction constants are given in Table III. Solution spectra of the palladium and platinum complexes showing the hyperfine splittings are given elsewhere.[6] In every case it was possible to generate these paramagnetic monoanions in the microwave cavity by controlled potential electrolysis[24] in acetonitrile or DMSO solution. The e.s.r. spectra

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[18] R. S. Nyholm and A. G. Sharpe, *J. Chem. Soc.*, 3579 (1952).

[19] N. Bartlett and K. Lohmann, *ibid.*, 5253 (1962).

[20] R. S. Nyholm, *ibid.*, 2061 (1950).

[21] R. Nast and T. von Krakkay, *Z. Naturforsch.*, **9b**, 798 (1954).

[22] E. O. Fischer and C. Palm, *Ber.*, **91**, 1725 (1958).

[23] H. C. Longuet-Higgins and A. J. Stone, *Mol. Phys.*, **5**, 417 (1962).

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

TABLE IV

CLASSIFICATION OF COMPLEXES ACCORDING TO PROBABLE ELECTRONIC STRUCTURES[a]

$(\pi_1^*)^2(\pi_2^*)^2(\sigma^*)^1$	$(\pi_1^*)^2(\pi_2^*)^2$	$(\pi_1^*)^2(\pi_2^*)^1$	$(\pi_1^*)^2$
$[CuS_4C_4(CN)_4]^{-2}$	$[CuS_4C_4(CN)_4]^-$	[b]	$[CoS_4C_4(CN)_4]^-$
	$[NiS_4C_4(CN)_4]^{-2}$	$[NiS_4C_4(CN)_4]^-$	
	$[PdS_4C_4(CN)_4]^{-2}$	$[PdS_4C_4(CN)_4]^-$	
	$[PtS_4C_4(CN)_4]^{-2}$	$[PtS_4C_4(CN)_4]^-$	
	$[AuS_4C_4(CN)_4]^-$		
	$[NiS_4C_4(C_6H_5)_4]^{-2}$	$[NiS_4C_4(C_6H_5)_4]^-$	$[NiS_4C_4(C_6H_5)_4]$
	$[NiS_4C_4(CF_3)_4]^{-2}$	$[NiS_4C_4(CF_3)_4]^-$	$[NiS_4C_4(CF_3)_4]$

[a] Complexes are assumed to be planar. [b] The anion $[CoS_4C_4(CN)_4]^{-2}$ is claimed to have an $S = {}^3/_2$ ground state[2] in which case a probable configuration is $(\pi_1^*)^1(\pi_2^*)^1(\sigma^*)^1$; however, recent work in this laboratory has shown that in reality this complex has an $S = {}^1/_2$ ground state with a probable configuration $(\pi_2^*)^1$. Full details of this work will be reported elsewhere.

were identical with those obtained from the chemically synthesized compounds.

In chloroform–dimethylformamide glasses at ~100°K. the paramagnetic monoanions display in all cases three well-separated g-values, reflecting marked departure of the ligand field from axial symmetry. Data for the R = CN series have already been quoted.[6] Typical are the results for $[NiS_4C_4(CN)_4]^-$: $g_1 = 1.996$, $g_2 = 2.043$, $g_3 = 2.140$. We defer detailed consideration of these results to a later report, but at present take note of the distinction between these data and those from glasses of typical planar d^9 Cu(II) complexes in which the in-plane anisotropy in the g-factor has not been resolved.[25] A highly pertinent comparison is with the related complex $[CuS_4C_4(CN)_4]^{-2}$ examined by Gray, Bernal, and Billig.[26] In a methanol glass only two g-values are observed. $g_{\parallel} = 2.0820$, $g_{\perp} = 2.0238$. This complex therefore possesses axial symmetry and, like typical d^9 cases, the odd electron is assigned to the σ^* (b_{1g}) molecular orbital. The paramagnetic monoanions examined in this work contain two less valence electrons than this complex and if they are planar, as is strongly suggested by the isomorphism studies, the electron configurations must be such as to yield a rhombic g-tensor. A detailed treatment of the magnetic anisotropy of these complexes will be given later. At present, preliminary investigations suggest the ordering of the molecular orbitals based on the metal d-orbitals in D_{2h} symmetry as

$$\sigma^* \ (b_{1g}) > \pi_2^* \ (b_{3g} \text{ or } b_{2g}) > \pi_1^* \ (b_{2g} \text{ or } b_{3g}) > \pi^* \ (a_g),\ \sigma^* \ (a_g)$$

Considering only the three highest molecular orbitals, we propose the classification scheme presented in Table IV. The rhombic symmetry of the g-tensor is consistent with the configurations $(\pi_1^*)^2(\pi_2^*)^1$, whereas near-axial symmetry would arise for $(\pi_1^*)^2(\pi_2^*)^2(\sigma^*)^1$. The π_1^* and π_2^* orbitals cannot be degenerate in this symmetry; otherwise, complexes such as $[CoS_4C_4(CN)_4]^-$ would be expected to be paramagnetic and exceedingly short spin-lattice relaxation times would be expected for complexes having the $(\pi^*)^3$ configuration.

TABLE V

CHARACTERISTIC LOW ENERGY ABSORPTION FEATURES OF COMPLEXES

Complex	Solvent	λ_{max}, cm.$^{-1}$	ϵ, l. mole^{-1} cm.$^{-1}$
$[CoS_4C_4(CN)_4]^-$	Acetone	14000, 12800	1200, 3700
$[NiS_4C_4(C_6H_5)_4]$	$CHCl_3$	11700	29800
$[NiS_4C_4(CF_3)_4]$	C_6H_{12}	13900	12400
$[NiS_4C_4(CN)_4]^-$	Acetone	11600	8000
$[PdS_4C_4(CN)_4]^-$	CH_2Cl_2	9000	13800
$[PtS_4C_4(CN)_4]^-$	Acetone	11700	11700
$[NiS_4C_4(C_6H_5)_4]^-$	CH_2Cl_2	10600	12500
$[NiS_4C_4(CF_3)_4]^-$	Acetone	12400	6480

Optical Spectra.—We mention here only those features of the spectra which are useful for purposes of identification and characterization. Complexes of the configurations $(\pi_1^*)^2(\pi_2^*)^1$ and $(\pi_1^*)^2$ possess an intense absorption band in the visible or near-infrared which is diagnostic for each species. Spectral data are given in Table V. This spectral feature is absent in complexes with the assigned configurations $(\pi_1^*)^2(\pi_2^*)^2$ and $(\pi_1^*)^2(\pi_2^*)^2(\sigma^*)^1$. The spectra of these dinegative anions are discussed elsewhere.[2,3]

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(25) See, for example, R. Petterson 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).

(26) H. B. Gray, I. Bernal, and E. Billig, to be published.