

ary, and tertiary, bind Hg(II) less well relative to protons than do other nitrogen bases. Bruehlman and Verhoek³ noted a similar effect with Ag(I) and secondary and tertiary amines.

Heterocyclic nitrogen compounds such as the purines, pyrimidines, and imidazole derivatives bind particularly strongly. However, other π -electron systems, such as aniline and pyridine, do not. The strong binding by the heterocycles may be due to donation of d-electrons from Hg⁺² into the π -electron system of the ring to place negative charge on the other nitrogen atoms. A similar but smaller effect would have been expected, but is not observed, for guanidine.

The slightly high value for ethylenediamine may be due to a small contribution from the formation of third and fourth bonds to Hg⁺². It is clear, however, that such chelate effects are very weak for Hg⁺² as compared to, say Cu⁺², because of the tendency of Hg⁺² to form two strong collinear bonds. The case of cycloserine may be complicated because there are two non-equivalent basic nitrogens in this molecule (in any case, the complex surely contains mercury-nitrogen bonds rather than mercury-oxygen bonds as suggested in ref. *k* of Table II).

We have drawn two lines in Fig. 2. The lower line is our suggestion as to the best correlation for typical amines without bulky alkyl substituents, and the upper line is for heterocyclic nitrogen compounds.

Acknowledgment.—This research has been supported by the Atomic Energy Commission under Contract

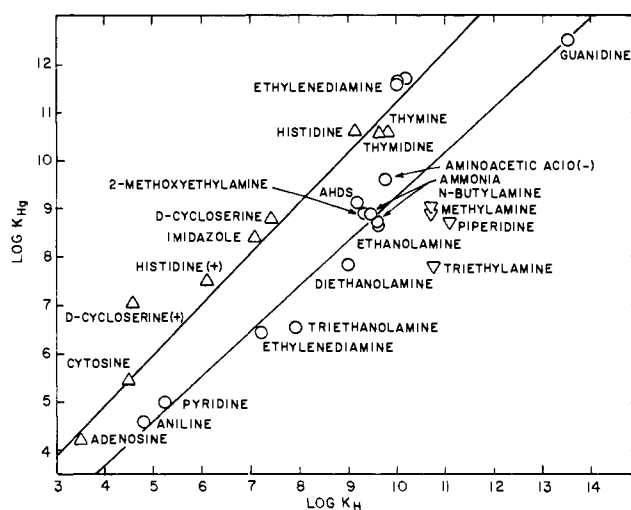


Fig. 2.—Complexes of Hg(II) with nitrogen bases; mean association constant (K_{Hg}) vs. proton affinity of the ligand (K_H) (AHDS = 2-amino-2'-hydroxydiethyl sulfide). Note that one of the points labeled ethylenediamine is for the singly protonated form. The two straight lines represent our suggestions for the best correlations for typical amines without bulky alkyl substituents (lower line) and for heterocyclic nitrogen compounds (upper line).

AT(11-1)-188. T. H. W. was a Woodrow Wilson Fellow in 1959–1960. We are indebted to Professor George S. Hammond for his optimistic attitude and helpful advice with regard to the interpretation of Fig. 2.

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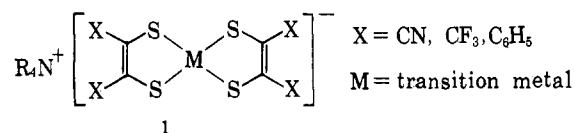
1,2-Dicyanoethylene-1,2-dithiolate Chelates

BY J. F. WEIHER, L. R. MELBY, AND R. E. BENSON

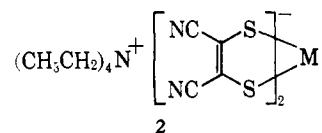
RECEIVED JUNE 15, 1964

Chelates derived from 1,2-dicyanoethylene-1,2-dithiol and certain transition metal ions exhibit singlet-triplet magnetic behavior which is attributed to spin interactions between pairs of metal ions through the sulfur atoms of adjacent ligands.

Dithiolate chelates 1 have been the subjects of



recent publications.¹⁻³ The work reported here deals with the solid-state magnetic properties of bis(1,2-dicyanoethylene-1,2-dithiolato) chelates (2) wherein



the metal ion formally has an odd-numbered d-electron configuration ($M = Fe, Ni, Pd, \text{ or } Pt$). From studies of the temperature dependence of their magnetic susceptibilities, we find that these complexes exist in a singlet ground state with a corresponding low-

lying triplet state. These studies, together with X-ray data on 2 ($M = Ni$) suggest that spin correlation occurs through sulfur atom d-orbital interaction with the metal ion of an adjacent chelate molecule.

The nickel monoanion (2, $M = Ni$) has been reported² to exist in a doublet state ($spin = 1/2$) in acetone solution. However, in the solid state the low magnetic moment (~ 1.0 B.M. at room temperature) indicated significant exchange demagnetization. The platinum chelate (2, $M = Pt$), in the solid state, was shown to be weakly paramagnetic (~ 1.1 B.M. at room temperature).²

The temperature dependence of the magnetic susceptibility for a system of doublet spins coupled into pairs by an antiferromagnetic interaction is given⁴ by

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \left[\frac{1}{3} e^{J/kT} + 1 \right]^{-1} + \chi_M^d + N\alpha \quad (1)$$

where J is the exchange coupling constant, g is the effective average splitting factor, χ_M^d is the underlying diamagnetic susceptibility, $N\alpha$ is the susceptibility due to temperature independent paramagnetism, β

(1) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963).

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

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

(4) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

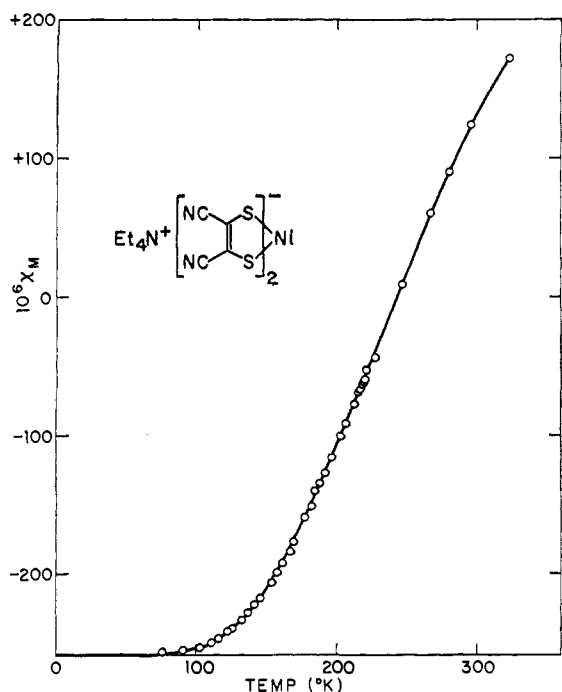


Fig. 1.—Temperature dependence of magnetic susceptibility for tetraethylammonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III): circles are experimental points; solid curve is theoretical dependence calculated with parameter values given in Table I.

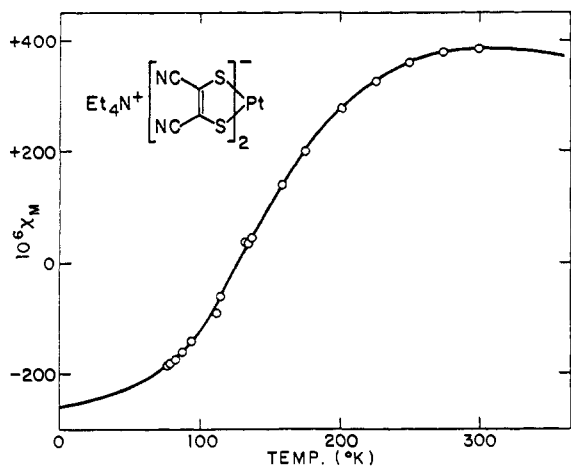


Fig. 2.—Temperature dependence of magnetic susceptibility for tetraethylammonium bis(1,2-dicyanoethylene-1,2-dithiolato)platinum(III): circles are experimental points; solid curve is theoretical dependence calculated with parameter values given in Table I.

is the Bohr magneton, k is the Boltzmann constant, and T is the absolute temperature. In Fig. 1 and 2, the experimentally determined relationships between temperature and magnetic susceptibility for the nickel monoanion ($2, M = \text{Ni}$) and the platinum monoanion ($2, M = \text{Pt}$) are compared with the theoretical values determined from eq. 1. The close agreement between the observed and calculated temperature dependences strongly suggests that the system involves a singlet ground state with a thermally accessible triplet state.

A multiplet equilibrium, however, can arise either from interactions between paramagnetic species or within them. The latter possibility is eliminated by observations on the nickel chelate in the magnetically dilute state. In the pure state, methyltriphenylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel-

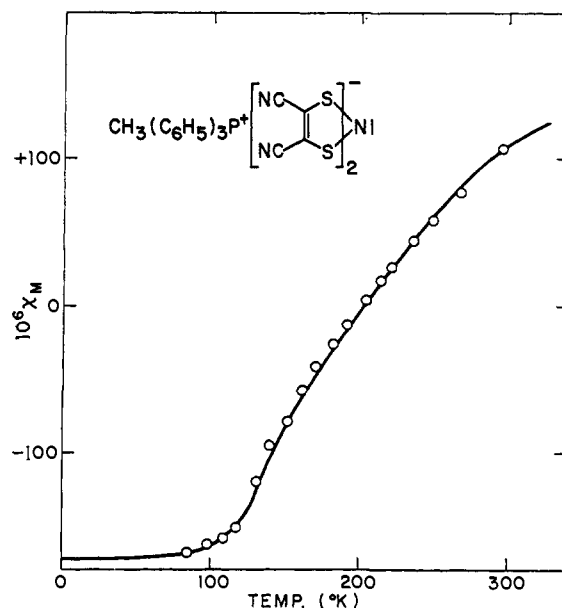


Fig. 3.—Temperature dependence of magnetic susceptibility for methyltriphenylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III): circles are experimental points; solid curve is theoretical dependence calculated with parameter values given in Table I.

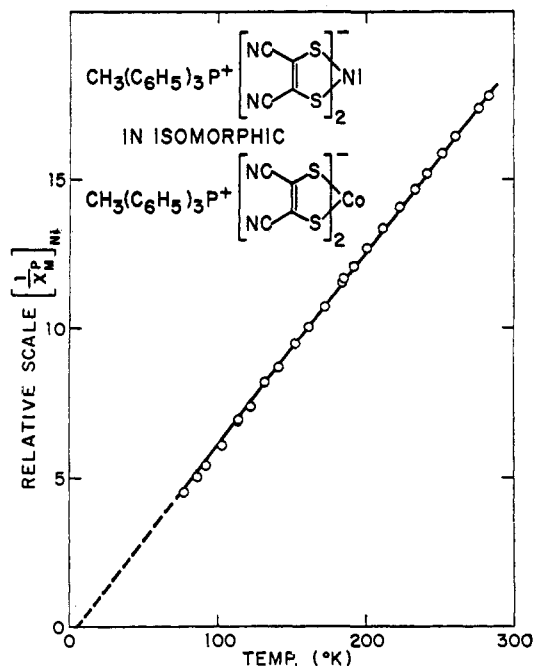


Fig. 4.—Temperature dependence of magnetic susceptibility for magnetically dilute methyltriphenylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III): circles are experimental points; solid curve drawn through points according to Curie-Weiss law.

(III) exhibits singlet-triplet behavior (Fig. 3), but when isomorphically substituted into the corresponding diamagnetic cobalt(III) chelate, it exhibits normal Curie-Weiss behavior (Fig. 4). Thus, the interactions producing the singlet-triplet equilibrium are *between* paramagnetic species.

On the basis of the close fit between the theoretical and experimentally determined temperature dependences of magnetic susceptibility, it is assumed that the paramagnetic centers are coupled into pairs. Furthermore, if long-range, cooperative interaction

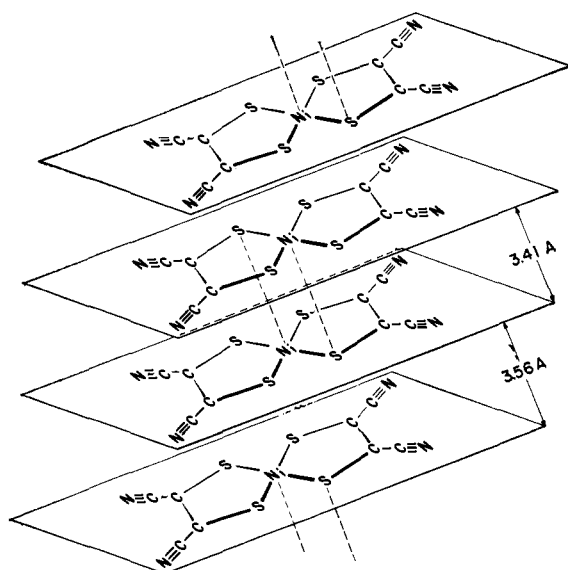


Fig. 5.—Monoanion orientation in methyltriphenylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III); see ref. 5.

was operative, a sharper inflection in the magnetic susceptibility curve would be expected; cf. Fig. 2.

Such a pairwise, rather than long-range or multi-center, interaction is in agreement with the crystal structure⁶ determination of one member of the series, *i.e.*, methyltriphenylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III). The nearly planar anions form staggered stacks in which each nickel has as nearest out-of-plane neighbors two sulfur atoms at distances of 3.59 and 3.75 Å. The magnetic interaction does not represent direct metal-metal bonding (Ni-Ni distance of 4.40 and 4.45 Å.), but rather spin correlation through an intermediate atom. The shortest nickel out-of-plane sulfur distance existing between pairs of layers is consistent with the assumption of a pairwise interaction (Fig. 5).

Assuming a square-planar ligand field and a low-spin d-electron configuration for the trivalent metal ions (d^5 or d^7), the isolated, *i.e.*, magnetically dilute, anions have a ground-state doublet. This electron configuration is in agreement with molecular orbital calculations⁸ for the corresponding dianion system.

Thus, in the Ni(III), Pt(III), and Pd(III) chelates **2**, the unpaired electron of an isolated anion is associated with the metal d_{xy} orbital. It is proposed that this spin is antiferromagnetically coupled to that of the other anion of a pair by (1) delocalization to an in-plane-bonded sulfur by $M d_{xy}$ -empty $S d_{xy}$ overlap, (2) polarization by spin exchange of the weak Ni-S bond that is formed by the interaction of the doubly occupied d_{z^2} orbital of the second nickel atom with the empty $S d_{z^2}$ orbital, and (3) correlation with the unpaired electron in the d_{xy} orbital of the second nickel atom by spin exchange. This view is schematically presented in Fig. 6. It should be noted that even though the Ni d_{z^2} -S d_{z^2} interaction is so small that increased stability of the system may be negligible, the extent of spin correlation may still be significant. In fact, the strength of the antiferromagnetic coupling is enhanced by the cooperation of two correlation paths per pair.

(5) C. J. Fritchie, Jr., to be published.

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

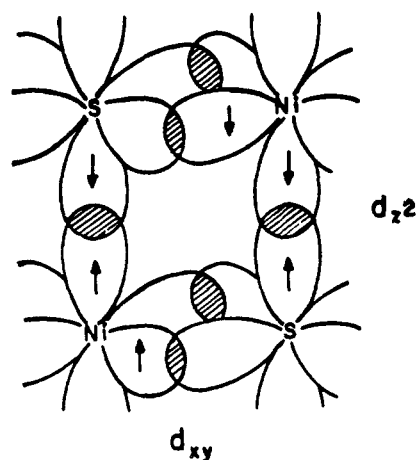


Fig. 6.—Schematic representation of proposed spin correlation mechanism in bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III) monoanion systems.

As in the π -complexes of the group VIII metals having the square-planar configuration, the system may be somewhat stabilized by the partial back donation of the Ni d_{z^2} pair and the Ni d_{xy} electron to the sulfur, thus compensating for the removal of charge from the S by the primary Ni-S bonding. On the basis of this model, the strength of the antiferromagnetic interaction coupling the doublets into singlet ground-state pairs should be quite sensitive to small changes in nickel-nearest out-of-plane sulfur distances. The effect of changes in metal atom and cation is given in Table I.

TABLE I
PAIRWISE INTERACTION PARAMETERS FOR
DITHIOLATE CHELATES

Chelate ^a	μ_{RT} , B.M.	J , cm.^{-1}	μ_T^b	$-(\chi_M^d + N\alpha)$
(Et ₄ N)Ni(III)L ₂ [(CH ₃)(C ₆ H ₅) ₃ P]- Ni(III)L ₂	0.96	620	3.7	260×10^{-6}
(Et ₄ N)Pt(III)L ₂	1.15	350	2.8	220×10^{-6}
(Et ₄ N)Pd(III)L ₂	Diamagnetic	>1000
(Et ₄ N)Fe(III)L ₂	1.62	300 ^c	3.4 ^c	...

^a L = S₂C₂(CN)₂. ^b μ_T = effective moment of triplet state = $g\sqrt{S(S+1)}$. ^c Based on an assumed pairwise interaction between doublet states.

The data in Table I show that the interaction J is quite sensitive to the nature of the cation, the ligand, and the metal ion for the d^7 systems. For the series Ni, Pd, and Pt in order of increasing size of the central metal ion, J goes through a maximum. Apparently, in the case of the Pd(III) chelate, the good overlap results in strong exchange with $J > 1000 \text{ cm.}^{-1}$, so that the compound is diamagnetic at room temperature, but for the smaller Ni(III) chelate and the larger Pt(III) chelate the overlap is significantly poorer, so that the compounds are paramagnetic at room temperature with lower values for the exchange constants.

Of all the chelates reported in Table I only the Fe(III) chelate deviates significantly from the pairwise antiferromagnetic interaction dependence of eq. 1. The magnetic susceptibility at room temperature corresponds to about 1.6 B.M., close to that expected for spin $1/2$.⁷ The moment decreases rapidly with decreasing temperature, qualitatively similar to the

(7) A spin of $3/2$ has been reported for bis(1,2-dicyanoethylene-1,2-dithiolato)iron⁻ with an unspecified cation, see ref. 1.

other members of the series, but the dependence does not so neatly fit the theoretical curve. Since a different electron configuration (d^5) is necessary for the Fe(III) compound, it is also possible that states higher than triplet are involved. In addition, deviations from theory may be the result of impurity effects. We have observed that with the nickel and platinum compounds extreme care must be taken during recrystallization procedures. If paramagnetic or ferromagnetic impurities are inadvertently introduced, significant deviations from the theoretically expected temperature dependence of the magnetic susceptibilities may result.

The tetraethylammonium salts of the Ni(III), Pd(III), and Pt(III) chelates were prepared by oxidation of the corresponding dianions in a manner similar to that also described by Davison, *et al.*³ The cobalt(III) chelate was prepared analogously, and the methyltriphenylphosphonium nickel(III) chelate was synthesized by oxidation of the corresponding dianion and by metathesis of the quaternary halide with sodium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III). Tetraethylammonium bis(1,2-dicyanoethylene-1,2-dithiolato)iron(III) was obtained from the reaction of ferric chloride with sodium 1,2-dicyanoethylene-1,2-dithiolate⁸ in the presence of tetraethylammonium bromide.

Experimental

Solid-state magnetic susceptibilities were measured with a Faraday balance using $\text{Hg}(\text{CNS})_4$ ⁹ as the calibrant.

Tetraethylammonium Bis(1,2-dicyanoethylene-1,2-dithiolato)iron(III).—To a solution of 1.86 g. of disodium 1,2-dicyanoethylene-1,2-dithiolate in 35 ml. of boiling ethanol was added a warm solution of 1.35 g. of ferric chloride hexahydrate in 20 ml. of ethanol. The solution was heated to boiling and filtered; to the filtrate was added a boiling solution of 2.10 g. of tetraethylammonium bromide in 15 ml. of ethanol. The black solution was allowed to stand at room temperature for 15 min., and the precipitate was then collected on a filter and washed with a little ice-cold ethanol. The yield of tetraethylammonium bis(1,2-dicyanoethylene-1,2-dithiolato)iron(III) was 1.25 g., m.p. ca. 280° dec.¹⁰

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{N}_5\text{S}_4\text{Fe}$: C, 41.2; H, 4.3; N, 15.0; S, 27.5; Fe, 12.0. Found: C, 41.5; H, 4.5; N, 15.4; S, 27.4; Fe, 11.7.

Methyltriphenylphosphonium Bis(1,2-dicyanoethylene-1,2-dithiolato)cobalt(II).—In 60 ml. of deaerated water was dissolved 2.1 g. of hydrated cobaltous chloride and 3.2 g. of disodium 1,2-dicyanoethylene-1,2-dithiolate. The solution was heated to about 60° under nitrogen, and a warm solution of 7.0 g. of methyltriphenylphosphonium iodide in a mixture of 25 ml. of water and 15 ml. of ethanol was added. The resulting black solid was collected on a filter under nitrogen, washed with water, and dried in air. It was recrystallized from a mixture of 80 ml. of acetonitrile and 175 ml. of ethanol to obtain 4.3 g. of brown crystals (after drying at 50° in a vacuum oven), m.p. 215–220° dec.

Anal. Calcd. for $\text{C}_{46}\text{H}_{36}\text{N}_4\text{P}_2\text{S}_4\text{Co}$: C, 61.8; H, 4.1; S, 14.3; Co, 6.6. Found: C, 61.6; H, 4.0; S, 14.3; Co, 6.7.

Methyltriphenylphosphonium Bis(1,2-dicyanoethylene-1,2-dithiolato)cobalt(III).—To a solution of 0.9 g. of the cobalt(II) compound in 30 ml. of boiling acetonitrile was added 0.15 g. of iodine in 15 ml. of boiling absolute ethanol. The mixture was cooled in ice, and the black crystalline solid was collected and washed on the filter with cold alcohol, yield 0.5 g., m.p. >230°.

Anal. Calcd. for $\text{C}_{27}\text{H}_{18}\text{N}_4\text{P}_2\text{S}_4\text{Co}$: C, 52.6; H, 2.9; S, 20.8; Co, 9.5. Found: C, 52.8; H, 3.1; S, 20.4; Co, 8.9.

Tetraethylammonium Bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(II).—In 25 ml. of water was dissolved 1.86 g. (10 mmoles) of disodium 1,2-dicyanoethylene-1,2-dithiolate and 2.10 g. of tetraethylammonium bromide. To the stirred solution was

added in small portions a solution of 1.20 g. of nickelous chloride hexahydrate in 10 ml. of water. The light orange solid was collected on a filter and then taken up in 150 ml. of boiling ethanol. The solution was filtered and cooled to 0° to obtain 2.3 g. (78% yield) of tetraethylammonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(II) as orange-red platelets, m.p. ca. 243–246° dec.

Anal. Calcd. for $\text{C}_{24}\text{H}_{40}\text{N}_6\text{S}_4\text{Ni}$: C, 48.1; H, 6.7; N, 14.0; Ni, 9.8. Found: C, 48.1; H, 6.6; N, 14.2; Ni, 9.8.

Sodium Bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III).—A solution of 3.72 g. of disodium 1,2-dicyanoethylene-1,2-dithiolate and 2.4 g. of nickel chloride hexahydrate in 50 ml. of water was slowly poured into a solution of 1.3 g. of iodine in 50 ml. of ethanol. The gray-green precipitate was collected on a filter, washed with water, and recrystallized from 100 ml. of ethanol to obtain 1.50 g. of sodium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III) as black crystals, m.p. >350°.

Anal. Calcd. for $\text{C}_8\text{N}_4\text{S}_4\text{NiNa}$: C, 26.7; H, 0.0; S, 35.4; Ni, 16.2. Found: C, 26.9; H, 0.2; S, 35.1; Ni, 16.2.

Methyltriphenylphosphonium Bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(II).—In 60 ml. of water was dissolved 3.70 g. of disodium 1,2-dicyanoethylene-1,2-dithiolate and 2.4 g. of nickel chloride hexahydrate. The solution was heated to boiling, and a boiling solution of 8.0 g. of methyltriphenylphosphonium iodide in a mixture of 50 ml. of water and 15 ml. of ethanol was added. The mixture was cooled to room temperature, and the orange-red solid was collected on a filter and washed with water. This product was air-dried and recrystallized from a mixture of 200 ml. of ethanol and 100 ml. of acetonitrile to obtain 6.3 g. of methyltriphenylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(II), m.p. ~220° dec.

Anal. Calcd. for $\text{C}_{46}\text{H}_{36}\text{N}_4\text{P}_2\text{S}_4\text{Ni}$: C, 61.8; H, 4.1; S, 14.3; Ni, 6.6. Found: C, 62.2; H, 4.2; S, 14.1; Ni, 6.6.

Methyltriphenylphosphonium Bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III).—In a boiling mixture of 20 ml. of ethanol and 15 ml. of acetonitrile was dissolved 0.9 g. of methyltriphenylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(II). The solution was filtered and kept boiling while a boiling solution of 0.15 g. of iodine in 15 ml. of ethanol was added. The mixture was allowed to stand at room temperature for 2 hr., and the long black needles were collected and washed on the filter with ethanol to obtain 0.4 g. of methyltriphenylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickel(III), m.p. 198–200° dec.

Anal. Calcd. for $\text{C}_{27}\text{H}_{18}\text{N}_4\text{P}_2\text{S}_4\text{Ni}$: C, 52.6; H, 2.9; S, 20.8; Ni, 9.5. Found: C, 52.9; H, 3.1; S, 20.9; Ni, 9.4.

Cocrystallization of the Cobalt(III) and Nickel(III) Chelates.—In a boiling mixture of 50 ml. of acetonitrile and 250 ml. of ethanol was dissolved 0.9 g. each of the methyltriphenylphosphonium cobalt(II) and nickel(II) chelates. The boiling solution was filtered, and a solution of 0.3 g. of iodine in 50 ml. of boiling ethanol was added. The mixture was allowed to stand at room temperature overnight. The black crystals were recovered by filtration and washed with ethanol. The yield was 0.7 g. Qualitative emission spectral analysis showed the presence of both nickel and cobalt with the latter predominating.

Tetraethylammonium Bis(1,2-dicyanoethylene-1,2-dithiolato)palladium(II).—In 50 ml. of deaerated water was suspended 0.89 g. of palladium dichloride, and 1.86 g. of disodium 1,2-dicyanoethylene-1,2-dithiolate was added. The mixture was stirred under a nitrogen atmosphere at room temperature for 2 days, filtered, diluted with 25 ml. of water, heated to boiling, and treated with a solution of 2.1 g. of tetraethylammonium bromide in 25 ml. of water. The green solid was collected on a filter and taken up in 100 ml. of boiling ethanol; the solution was filtered and cooled in a wet ice-acetone bath to obtain 1.15 g. (35% yield) of tetraethylammonium bis(1,2-dicyanoethylene-1,2-dithiolato)palladium(II) as green platelets, m.p. ca. 240° dec.

Anal. Calcd. for $\text{C}_{24}\text{H}_{40}\text{N}_6\text{S}_4\text{Pd}$: C, 44.5; H, 6.2; N, 13.0; Pd, 16.5. Found: C, 44.8; H, 6.2; N, 12.9; Pd, 16.5.

Tetraethylammonium Bis(1,2-dicyanoethylene-1,2-dithiolato)platinum(II).—A mixture of 5.0 g. of dipotassium platinumous chloride (K_2PtCl_4 , Fisher Scientific Co.) and 4.5 g. of disodium 1,2-dicyanoethylene-1,2-dithiolate in 50 ml. of deaerated water was heated to boiling, and a solution of 5.1 g. of tetraethylammonium bromide in 25 ml. of water was added. The mixture was filtered while hot, and the red filter cake was washed with water and air-dried. The crude solid was recrystallized from ethanol to obtain 4.7 g. (53% yield) of bis(tetraethylammonium) bis(1,2-dicyanoethylene-1,2-dithiolato)platinum(II) in the form of red flakes, m.p. 242–246° dec.

(8) G. Bähr and G. Schleiter, *Ber.*, **88**, 1771 (1955); **90**, 438 (1957).

(9) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(10) Melting points and decomposition points are uncorrected.

Anal. Calcd. for $C_{26}H_{40}N_6S_4Pt$: C, 39.4; H, 5.4; N, 11.4; Pt, 26.5. Found: C, 39.1; H, 5.5; N, 11.3; Pt, 27.1.

Tetraethylammonium Bis(1,2-dicyanoethylene-1,2-dithiolato)-metal(III) Chelates.—The oxidized forms of the nickel, palladium, and platinum chelates were prepared by iodine oxidation of

the reduced forms essentially according to the directions previously described.³

Acknowledgments.—We wish to thank Drs. D. R. Eaton, C. J. Fritchie, Jr., M. Thomas Jones, and R. G. Kepler for helpful discussions.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER COMPANY, WILMINGTON, DELAWARE]

The Electrochemistry of Inorganic Difluoramino Compounds. I. The Mechanism of the Electrochemical Oxidation of Difluoramine and the Use of this Reaction in the Synthesis of Alkyl Difluoramines

BY GEORGE A. WARD AND CHARLES M. WRIGHT

RECEIVED MAY 8, 1964

The mechanism of the anodic oxidation of difluoramine on platinum electrodes has been studied using the techniques of cyclic voltammetry, coulometry, and chronopotentiometry. The reaction has been shown to be pH dependent, irreversible, kinetically controlled, and strongly dependent on the oxidation state of the electrode. The primary product of the electron transfer, which involves the loss of one electron per difluoramine molecule, is the difluoramino radical, $\cdot NF_2$. If no other radicals are present at the electrode surface, the difluoramino radicals rapidly combine to form tetrafluorohydrazine. In the presence of simultaneously generated alkyl radicals, however, the difluoramino radicals have been shown to react to form alkyl difluoramines according to the reaction $R\cdot + \cdot NF_2 \rightarrow RNF_2$. In this manner, CH_3NF_2 , $CH_3CH_2NF_2$, and CD_3NF_2 have been prepared.

The chemistry of the $-NF_2$ group is of considerable current interest, and several comprehensive reviews of the chemistry of difluoramino compounds have recently appeared.¹⁻³ To date, however, no investigation of the electrochemistry of these compounds has been reported.

As part of an integrated study of the electronic configuration and behavior of the difluoramino group,⁴ we are currently investigating the electrochemical reactions of the inorganic difluoramino compounds. The present paper describes a study of the anodic oxidation of difluoramine and the use of this reaction in the synthesis of alkyl difluoramino compounds.

Results and Discussion

Mechanism of the Anodic Oxidation of Difluoramine.

—The anodic cyclic voltammetry of HNF_2 was studied over the pH range 0.7 to 10.3 in aqueous buffer systems, using a planar platinum electrode. In acidic systems ($pH \leq 6.85$), HNF_2 was found to undergo an irreversible oxidation which takes place at a potential dependent on the pH of the system. In basic systems the HNF_2 was converted to N_2F_2 , and no oxidation waves were observed over the voltage range 0 to ± 1.2 v. vs. s.c.e.

Typical cyclic voltammetric scans are shown in Fig. 1 and 2 for the oxidation of HNF_2 in 0.2 M $HClO_4$ and a 1.0 M acetic acid-sodium acetate buffer of pH 4.8, respectively. Accurate measurement of the peak potential of the wave (E_p) is not possible owing to the shape of the current-voltage curve for these irreversible oxidations. The variation of the half-peak potential ($E_{p/2}$), however, which may be more accurately estimated, clearly shows the position of the waves on the voltage axis to be pH dependent. In addition, although $E_{p/2}$ varies from +0.61 v. in the $HClO_4$ system (pH 0.7) to 0.37 v. in the acetic acid system, the height

of the diffusion current wave (i_p) is the same in both cases, within experimental error, suggesting that there is no change in the number of electrons involved in the oxidation, or in the electroactive species, over this pH range. The variation of i_p with the square root of the voltage scan rate ($V^{1/2}$) and the concentration of HNF_2 (C_{HNF_2}) in the bulk of the electrolysis solution was studied in both systems and, as shown in Fig. 3 and 4, plots of i_p vs. $V^{1/2}$ and i_p vs. C_{HNF_2} were found to be linear over the limited range studied. Thus the oxidation appears to be diffusion controlled under these conditions.

The over-all irreversibility of the oxidation is suggested by several observations. First, the current-voltage curve of the anodic scan in cyclic voltammetry has a drawn-out shape rather than the sharp peak normally exhibited by a reversible electrode reaction. Second, in a reversible oxidation, the product of the electrode reaction should give a cathodic reduction peak on the reverse sweep of the cyclic scan, at a potential near that at which the oxidation takes place. For a completely reversible process, the difference between the anodic and cathodic peak potentials should be $0.056/n$ v., in which n is the number of electrons involved in the oxidation. For irreversible processes, the difference between cathodic and anodic peaks is larger. Since no cathodic peak is observed for HNF_2 , at least within 0.5 v. of the oxidation peak, the over-all reaction at the electrode surface appears to be irreversible. Finally, in current reversal chronopotentiometric studies of the reaction, no transition time for reduction of the product of the oxidation of HNF_2 was observed when the polarity of the current was reversed at the transition time for the oxidation process. This over-all irreversibility, however, may be due to an irreversible chemical reaction in which the product of the primary electrolysis reaction is rapidly converted to a nonelectroactive species, as well as to an irreversible electrode reaction.

Controlled potential microcoulometric determinations showed that one electron per HNF_2 molecule is involved in the electrode reaction.

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