months in the absence of air. When III was treated with an entire mole of iodine, the initially formed radical cation disappeared and an orange-red solution remained. Concentration caused the solution to deposit orange-red crystals of the di-iodide of V formed by transfer of a second electron to iodine. Purified by recrystallization from acetonitrile, the diiodide melted at 294–295°.
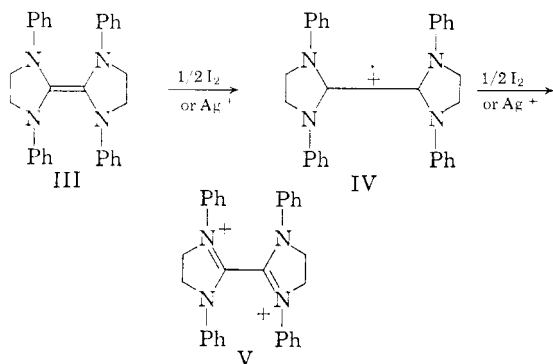
In a similar fashion, oxidation of III by silver nitrate in acetonitrile could be carried out in two discrete stages.[3] The violet color due to IV faded upon addition of a second equivalent of silver ion, leaving a yellow solution of the dinitrate. Canary yellow prisms of the dinitrate were obtained from acetonitrile/benzene (m.p. 242–243°). The corresponding diperchlorate was prepared from the ethylene III with silver perchlorate as the oxidizing agent (canary yellow crystals from acetonitrile, m.p. 341–342°).[4] *Anal.* Calcd. for $C_{30}H_{28}Cl_2N_4O_8$: C, 55.99; H, 4.38; N, 8.71. Found: C, 55.71; H, 4.63; N, 8.60. The disalts could be inter-converted readily
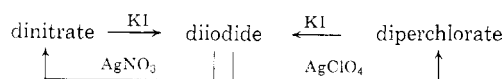
Aqueous base rapidly cleaved the dinitrate into the two anticipated fragments, 1,3-diphenylimid-azolid-2-one and N-formyl-N,N'-diphenylethylene-diamine; they were isolated pure in 77 and 79% yield, respectively.

It is striking that the radical cation IV was formed when an acetonitrile suspension of III was treated with any one of the three disalts, thus demonstrating that electron abstraction from IV is freely reversible. Addition of excess iodide ion to a suspension of the diiodide failed to reverse the equilibria III $\rightleftarrows$ IV $\rightleftarrows$ V, but finely-divided silver proved to be a sufficiently powerful reducing agent in the presence of iodide ion to transform any of the disalts first to IV and then to III.

The e.s.r. spectrum of IV in chloroform is remarkable for its simplicity. From the analogy of IV to a Wurster cation, one would anticipate that the spin density of the unpaired electron would be large at the four nitrogen nuclei and quite likely measurable

(3) These iodine and silver ion oxidations parallel the experiments of D. H. Anderson, *et al.*, with tetrakis-(*p*-dimethylaminophenyl)-ethylene, *J. Am. Chem. Soc.*, **83**, 3157 (1961).

(4) All melting points are uncorrected. For the dinitrate, di-perchlorate and diiodide salts it has been demonstrated that the melting points are strongly dependent upon the mode of recrystallization.

at the aromatic ring protons as well. Hyperfine splitting by the nitrogens alone would produce a nine line multiplet, but the observed spectrum consists of a single broad line (5.4 gauss at maximum slope) at $g = 2.0057 \pm 0.0001$. Although this suggests that the unpaired electron is localized on the central carbons, a simple LCAO-MO calculation for the tetraaminoethylene system strongly supports the idea that the delocalization energy of IV and the spin densities at nitrogen are large. That the absorption line shape for our dilute solutions is strictly Gaussian, not Lorentzian, appears to exclude the possibility that exchange interaction[5] is compressing the band width and obliterating fine structure.

Acknowledgment.—The authors wish to express their appreciation to Professors E. M. Kosower and R. West for helpful discussions, to Professor West and Mr. C. M. Lang for measuring the e.s.r. spectra, and to the National Science Foundation for financial assistance.

(5) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Academic Press, Inc., New York, N. Y., 1958, Chap. 4; D. Kivelson, *J. Chem. Phys.*, **27**, 1087 (1957).

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RECEIVED MARCH 7, 1962

REACTIONS OF COÖRDINATED LIGANDS. II. NICKEL(II) COMPLEXES OF SOME NOVEL TETRADENTATE LIGANDS

Sir:

The area of "Reactions of Coördinated Ligands" is a new one and it is of that peculiar nature which should be of interest to chemists in a variety of fields. This communication provides a dramatic example of the role played by a metal ion in facilitating the formation of an organic molecule that is otherwise strongly discriminated against by competing reactions. In effect, the metal ion brings the reactants together in the product form that is most favorable for complexation.

The substances of immediate concern are the Schiff bases formed between α-diketones and β-mercaptoethylamine. Attempts to synthesize materials of this class by obvious routes yield thiazo-lines as major products, with some evidence for the formation of mercaptals and the desired α-diimines in low yields.

The structures of the diimines formed between α-diketones and β-mercaptoethylamine are steri-cally well suited to chelate in a tetradentate manner with square planar metal ions. In the design of these experiments, the coördination sphere of the metal ion is considered to serve as a slightly flexible template within which the coördination positions are in juxtaposition to the functional groups of the protracted ligand molecule. The chelate rings are expected to greatly stabilize the system for the complexing ability of the α-diimine linkage is well established[1,2] and recent work in these laboratories has led to the characterization of many planar

(1) P. E. Figgins and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 820 (1960).

(2) P. E. Figgins and D. H. Busch, *J. Phys. Chem.*, **65**, 2236 (1961).

complexes involving the β-mercaptoethylamine grouping.[3] On this basis it is reasonably suggested that the metal ion may bring together the diketone and two moles of mercaptoethylamine in a manner such that the reaction product achieves the predicted form.

When the reactions are carried out in the presence of nickel(II) ion, yields of greater than 70% of the easily purified Schiff base complexes (structure I) are obtained.

I
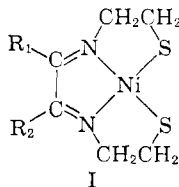
The complexes which have been prepared are biacetyl-bis-(mercaptoethylimine)-nickel(II), 2,3-pentanedione - bis - (mercaptoethylimine) - nickel-(II), 2,3-octanedione-bis-(mercaptoethylimine)-nickel(II), and 1-phenyl-1,2-propanedione-bis-(mercaptoethylimine)-nickel(II). These compounds shall be abbreviated as Ni(BE), Ni(PE), Ni(OE), and Ni(PPE), respectively.[4]

Anal. Calcd. for Ni(BE): C, 36.81; H, 5.41; N, 10.73; S, 24.57. Found: C, 36.74; H, 5.53; N, 10.72; S, 24.37. Calcd. for Ni(PE): C, 39.30; H, 5.86; N, 10.19; S, 23.31. Found: C, 39.34; H, 5.84; N, 10.18; S, 23.19. Calcd. for Ni(OE): C, 45.44; H, 6.99; N, 8.84; S, 20.22. Found: C, 45.31; H, 6.92; N, 8.68; S, 20.02.

The infrared spectra of these complexes show the absence of the strong N–H and carbonyl absorptions, and the presence of a weak absorption corresponding to the stretching vibration of the carbon–nitrogen double bond. This is consistent with the proposed structure. Ni(BE), Ni(PE) and Ni(OE) are diamagnetic, and may therefore be assumed to exist in the expected planar form.

These substances are slightly soluble in a variety of solvents, including benzene, substituted benzenes, halocarbons, alcohols, and water. Molecular weight determinations are hampered by the limited solubilities; however, the measured values agree, within the experimental uncertainties, with the monomer values. *Mol. wt.* Calcd. for Ni(BE), 261; found, 290. Calcd. for Ni(OE), 317; found, 318.

The visible spectra exhibit the usual ligand field transition predicted for *cis*-planar nickel(II).[5] The band occurs at about 430 mμ, in all cases, supporting the expectation that these ligands should exhibit greater ligand field strengths than those associated with nitrogen and oxygen donors. In addition to the ligand field transition, the visible spectra reveal a much more intense absorption

maximum which shifts with change of solvent. In the case of Ni(BE) the band maximum ranges from 486 mμ (H$_2$O) to 580 mμ (CS$_2$). The extinction coefficients vary from 1.5×10^3 to 10^4. It is apparent that the shift of the band does not correlate with the coördinating ability of the solvent, since, for example, pyridine, a solvent of strong coördinating tendency, produces a shift comparable to that due to the halocarbons, which are very poor coördinating agents. A more successful correlation has been obtained through the use of Kosower's[6] solvent polarity parameter, Z. The complete results of these continuing investigations will be published in greater detail elsewhere. The template hypothesis is presently being tested by application to other reactions.

Acknowledgment.—The financial support of the National Institutes of Health is gratefully acknowledged.

(6) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

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ORGANOSILYL AZIDES

Sir:

We wish to report the synthesis of the first organosilicon azides. In common with many other azides,[2-4] these substances were expected to have low thermal stability. Surprisingly, one of these compounds, azidotriphenylsilane (I), is remarkably resistant to heat, being only 50% destroyed after ten hours at 220° in *n*-hexadecane solution. It appears to be more stable to heat than any previously known covalent azide.

The organosilyl azides were prepared from the corresponding chlorosilanes and a sodium azide–aluminum chloride mixture in refluxing tetrahydrofuran. Recrystallization from *n*-hexane gave colorless crystals of I (m.p. 81°) in 90% yield. I is insoluble in water but readily soluble in most organic solvents. *Anal.* Calcd. for C$_{18}$H$_{15}$N$_3$Si: C, 71.72; N, 13.94; H, 5.02; mol. wt., 301. Found: C, 71.50; N, 13.89; H, 5.16; mol. wt., 286. Azidophenyldimethylsilane was isolated as a colorless liquid, b.p. 70° (0.15 mm.). It was analyzed by hydrolysis and titration of the liberated hydrazoic acid. *Anal.* Calcd. for C$_8$H$_{11}$N$_3$Si: eq. wt., 177.2; found: eq. wt., 176. Azidotrimethylsilane was obtained by a similar reaction using bis-(2-methoxyethyl) ether as solvent. It is a volatile liquid that has to date been isolated only in 90% purity.

Qualitative estimates of hydrolysis rates of the silyl azides in aqueous acetone were made by observing the development of the deep red color of the Fe^{+3}-azide complex. All three azides

(3) D. C. Jicha and D. H. Busch, 135th Meeting of the American Chemical Society, Atlantic City, 1959.

(4) The International Union names for these compounds are, respectively, 2,2'-dimethyl(ethanediylidenedinitrilo)diethanethiolonickel(II); 2 - methyl - 2' - ethyl(ethanediylidenedinitrilo)diethanethiolonickel(II); 2 - methyl - 2' - pentyl(ethanediylidenedinitrilo)diethanethiolonickel (II); and 2-methyl-2'-phenyl(ethanediylidenedinitrilo)diethanethiolonickel(II).

(5) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958).

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285 and grant No. AF-AFOSR-62-244. Reproduction in whole or part is permitted for any purpose of the United States Government.

(2) A. Bertho, *Ber.*, **57**, 1138 (1924).

(3) W. H. Saunders and J. C. Ware, *J. Am. Chem. Soc.*, **80**, 3328 (1958).

(4) G. Smolinsky, *ibid.*, **82**, 4717 (1960); **83**, 2489 (1961).