account in this figure. However, even according to this estimate, ΔH has the same sign in pure alcohol as in water. It is therefore impossible to explain the reversal of the temperature effect in Fig. 10 by assuming that $Thio_2^{++}$ becomes endothermal in strongly alcoholic solutions. The "negative" temperature effect in alcohol cannot therefore be due to the dimerization equilibrium; we may attribute it instead to the dissociation of the $ThioA^+$ complexes, or it may be simply the effect of increased rotation and collision frequency, which often causes a lowering and broadening of absorption bands with increasing temperature.

Summary

1. Extinction curves of thionine and methylene blue were determined at different concentrations and temperatures, in water, ethanol and ethanol–water mixtures.

2. In water, deviations from Beer's law appear even at the lowest concentrations ($<10^{-6}$ mole/liter) and can be explained quantitatively by the formation of dimeric ions $Thio_2^{++}$ and MB_2^{++}. Dissociation constants and the heats and entropies of formation of the dimers are calculated.

3. Dimerization does not occur in pure ethanol, and it is reduced considerably in alcohol–water mixtures.

4. Dimeric ions do not fluoresce; self-quenching of fluorescence at the higher concentrations of the dyestuff is due to dimerization. No self-quenching occurs in alcohol.

5. Other properties of dyestuff solutions (oxidation–reduction potentials, conductivity, osmotic pressure, etc.) are in accord with the dimerization hypothesis.

6. Dimerization (and higher polymerization) is a universal property of organic dyestuffs, fundamentally associated with the property of color. It can be interpreted quantitatively on the basis of London's theory of intermolecular forces.

7. Potential energy curves are constructed for the interaction of two $Thio^+$ ions in water and in ethanol. Because of the coulombic repulsion between ions of the same sign, dimerization is found to require an activation energy.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TECHNICAL COLLEGE, SYDNEY]

Chelation in Metallic Triazene Salts

BY F. P. DWYER

Recently it was shown that if the silver salt of the *aci* form of 4-nitrodiazoaminobenzene was allowed to revert to the triazene form, and then methylated, instead of the expected N-methyl derivative with the methyl group adjacent to the nitro group, a mixture of equal amounts of N-methyl-4-nitrodiazoaminobenzene and N-methyl-4′-nitrodiazoaminobenzene resulted.[1] This suggested that the silver salt of the triazene form exhibited dynamic isomerism or, more probably, could be best formulated as an internal complex in which the triazene group acted as a chelate group.

In order to obtain more adequate support for the latter view, a number of other metallic complexes with diazoaminobenzene and 4,4′-dimethyldiazoaminobenzene have been examined. The complexes showed the ready solubility in organic media that is characteristic of covalent compounds. The molecular weights in most instances were normal, and from coördination experiments with ethylenediamine and pyridine the chelating function of the triazene group seems definitely indicated.

Experimental

Since most preparations of diazoamino compounds contain traces of diazoaminoazo compounds that have led to much confusion in the chemistry of diazoamino compounds, the diazoaminobenzene and 4,4′-dimethyldiazoaminobenzene were specially purified. The pure lemon-yellow compounds melted at 100 and 119°, respectively.[2]

Palladium Complexes with Diazoaminobenzene.—A cold solution of sodium chloropalladite, 35 ml. containing 1.06 g. of palladium, mixed with 15 ml. of sodium acetate solution (3 *N*) and added rapidly to an ice-cold solution of diazoaminobenzene, 3.94 g. in methanol, 100 ml., gave a voluminous precipitate of **tris-diazoaminobenzenepalladium** (I). After washing with 80% methanol the substance was dissolved in ice cold acetone, filtered as rapidly as possible, and immediately precipitated with ice water. The resulting unstable brown powder was extremely soluble in all organic solvents and even petroleum ether to

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[1] F. P. Dwyer, *J. Australian Chem. Inst.*, **6**, 362 (1939).

[2] F. P. Dwyer, *J. Soc. Chem. Ind.*, **56**, 70 (1937).

intense reddish-brown solutions. The compound melted at 120–125° with decomposition. Owing to the ease with which one molecule of diazoaminobenzene is lost, the pure compound could not be obtained.

Anal. Calcd. for $Pd(C_{12}H_{10}N_3)_2 \cdot C_{12}H_{10}N_3H$: Pd, 15.33. Found: Pd, 16.00.

Dissolved in ice-cold pyridine, then precipitated with water, one molecule of the triazene was replaced, and *bis*-**pyridine**-*bis*-**diazoaminobenzenepalladium** (II) was precipitated as an oil which soon crystallized to orange clusters of cruciform needles. The compound was easily soluble in benzene and acetone.

Anal. Calcd. for $Pd(C_{12}H_{10}N_3)_2 \cdot 2C_5H_5N$: Pd, 16.25; C_5H_5N, 24.06. Found: Pd, 16.35; C_5H_5N, 24.13.

Treated in warm benzene with anhydrous ethylenediamine (1 mole), tris-diazoaminobenzenepalladium again lost one molecule of triazene, and on the addition of petroleum ether **mono-ethylenediamine**-*bis*-**diazoaminobenzenepalladium** (III) was precipitated as a yellowish-brown powder.

Anal. Calcd. for $Pd(C_{12}H_{10}N_3)_2 \cdot C_2H_8N_2$: Pd, 19.10. Found: Pd, 19.20.

Solutions of tris-diazoaminobenzenepalladium when allowed to stand at room temperature, or preferably if the acetone solution was warmed to 50°, gave *bis*-**diazoaminobenzenepalladium** (IV) as a brown precipitate. Crystallized from benzene and petroleum ether it gave small flat reddish-brown plates, insoluble in alcohol and acetone but easily soluble in warm benzene and chloroform. The compound decomposed above 300° with incandescence. It could be crystallized from pyridine without any coördination occurring, nor could ethylenediamine be coördinated. The original tris-diazoaminobenzenepalladium could not be regenerated by the action of even saturated solutions of diazoaminobenzene on the bis-diazoaminobenzenepalladium compound.

Anal. Calcd. for $Pd(C_{12}H_{10}N_3)_2$: Pd, 21.39; N, 16.85; mol. wt., 499. Found: Pd, 21.37; N, 16.9; mol. wt. ebullioscopic in benzene, 587, 602.

Palladium Complexes with 4,4′-Dimethyldiazoaminobenzene.—Reaction between sodium chloropalladite and the triazene as before in the presence of sodium acetate gave **tris-4,4′-dimethyldiazoaminobenzenepalladium** (V) as an unstable brown powder easily soluble in organic solvents.

Anal. Calcd. for $Pd(C_{14}H_{14}N_3)_2 \cdot C_{14}H_{14}N_3H$: Pd, 13.68. Found: Pd, 13.23.

Tris-4,4′-dimethyldiazoaminobenzene palladium warmed in acetone solution gave a brown precipitate of *bis*-**4,4′-dimethyldiazoaminobenzenepalladium** (VI), which crystallized from benzene in reddish-brown plates. The compound decomposed violently without melting above 300°, could be crystallized unchanged from pyridine and did not react with ethylenediamine.

Anal. Calcd. for $Pd(C_{14}H_{14}N_3)_2$: Pd, 19.16; N, 15.16; mol. wt., 554. Found: Pd, 19.18; N, 15.3; mol. wt. ebullioscopic in benzene, 545, 576.

Cupric Compounds with Diazoaminobenzene.—*Bis*-**diazoaminobenzenecopper** (VII) has been described previously,[3] but the compound was probably contaminated with bis-diazoaminoazobenzene-copper. The pure complex, prepared by the addition of methyl alcoholic cupric acetate (1 mole) to an ice-cold methyl alcoholic solution of the triazene, and crystallized from benzene and petroleum ether, gave shining dark green dendritic needles. The complex decomposed violently at 120–130°. In warm alcoholic solution nitrogen was evolved and a tar resulted, but in cold inert solvents such as benzene or chloroform the dark green solution underwent rapid self-reduction to an orange-brown solution of the cuprous compound. For this reason the molecular weight determinations were somewhat uncertain.

Anal. Calcd. for $(C_{12}H_{10}N_3)_2 \cdot Cu$: Cu, 13.95; mol. wt., 455. Found: Cu, 13.89; mol. wt. in bromoform, 575, 662.

Dissolved in cold benzene, treated with pyridine (2 moles) and shaken for one minute, the compound (VII) underwent no change and could be recovered. However, when dissolved in hot pyridine and carefully precipitated with water it gave indigo blue needles of *bis*-**pyridine** *bis*-**diazoaminobenzenecopper** (VIII). The compound lost pyridine at 100–120°, becoming transformed smoothly into the cuprous compound.

Anal. Calcd. for $(C_{12}H_{10}N_3)_2 \cdot Cu \cdot 2C_5H_5N$: Cu, 10.36; C_5H_5N, 25.75. Found: Cu, 10.39; C_5H_5N, 25.87.

Bis-diazoaminobenzenecopper failed to react with ethylenediamine (1 mole) in ice-cold benzene, but on warming to 40° the color changed to brown, and addition of petroleum ether gave dark greenish-brown needles of **mono-ethylenediamine bis-diazoaminobenzene copper** (IX). The compound lost one molecule of benzene "of crystallization" at 90–100°, melted at 140–143°, and at 145° a gas was evolved and the cuprous salt formed.

Anal. Calcd. for $(C_{12}H_{10}N_3)_2 \cdot Cu \cdot C_2H_8N_2 \cdot C_6H_6$: Cu, 10.71; C_6H_6, 13.14. Found: Cu, 10.78; C_6H_6, 13.41.

Cupric Compounds with 4,4′-Dimethyldiazoaminobenzene.—Methyl alcoholic solutions of the triazene and cupric acetate as before gave bis-4,4′-dimethyldiazoaminobenzenecopper, green plates from benzene and petroleum ether.

Anal. Calcd. for $(C_{14}H_{14}N_3)_2 \cdot Cu$: Cu, 12.43. Found: Cu, 12.30.

Dissolved in hot pyridine and precipitated with water it gave bis-pyridine-bis-4,4′-dimethyldiazoaminobenzenecopper as indigo blue needles.

Anal. Calcd. for $(C_{14}H_{14}N_3)_2 \cdot Cu \cdot 2C_5H_5N$: Cu, 9.78; C_5H_5N, 24.62. Found: Cu, 9.79; C_5H_5N, 24.53.

Bis-pyridinediazoaminobenzenecopper (X).—Cuprous chloride, 1.9 g. (1 mole), was dissolved in 15 ml. of pyridine at 100°, in the absence of air, and added immediately to diazoaminobenzene, 4.0 g. (1 mole), in 50 ml. of warm alcohol. Sodium hydroxide solution (2 *N*), 10 ml., was added while stirring rapidly. The initial orange precipitate soon changed to yellow, and after filtration was dissolved in hot pyridine. Rapid cooling of the solution gave lemon-yellow needles of the compound. The coördinated pyridine was lost easily by washing with alcohol or acetone, or could be eliminated at 100°.

Anal. Calcd. for $(C_{12}H_{10}N_3) \cdot Cu \cdot 2C_5H_5N$: Cu, 15.23; C_5H_5N, 37.84. Found: Cu, 15.27; C_5H_5N, 37.34.

Elimination of the pyridine at 100° gave pure **diazoaminobenzenecopper** (XI) as a lemon-yellow powder,

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(3) A. Mangini and I. Dejudicibus, *Gazz. chim. ital.*, **63**, 1 (1933).

moderately soluble in benzene and chloroform to orange-yellow solutions. The compound melted at 280°, and appeared to be dimorphous. An orange-red form could be obtained by addition of petroleum ether to the benzene solution.

Anal. Calcd. for $(C_{12}H_{10}N_3)\cdot Cu$: Cu, 25.06; mol. wt., 259. Found: Cu, 25.12; mol. wt. in benzene ebullioscopic, 279, 293.

Silver Triazene Complexes.—Diazoaminobenzenesilver (XII) most probably in an impure form has already been described.[4] The pure compound was prepared by the addition of bis-pyridine silver acetate (1 mole) to a methyl alcoholic solution of the triazene. Crystallized from hot pyridine it gave lemon-yellow needles. The compound was only very slightly soluble in all solvents except warm nitrobenzene. Under no conditions could it be induced to coördinate with ammonia, ethylenediamine, pyridine or thiocarbamide. The molecular weight determined in pyridine by Rast's modification[5] of Barger's method was normal.

Anal. Calcd. for $(C_{12}H_{10}N_3)Ag$: Ag, 35.50. Found: Ag, 35.52.

4,4'-Dimethyldiazoaminobenzenesilver (XIII) prepared similarly gave lemon-yellow needles from pyridine, and resisted all efforts at coördination. The molecular weight in pyridine was normal.

Anal. Calcd. for $(C_{14}H_{14}N_3)Ag$: Ag, 32.51. Found: Ag, 32.49.

Molecular Weights of the Pure Triazenes.—These were determined cryoscopically in benzene. Concentrations are expressed in grams of solute in 100 g. of solvent.

Diazoaminobenzene, calcd. mol. wt., 197

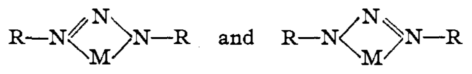
Concn.	1.12	1.78	2.40	3.97
Mol. wt. obsd.	197.6	201	202	213

4,4'-Dimethyldiazoaminobenzene, calcd. mol. wt., 225

Concn.	1.05	2.12	2.80	3.32
Mol. wt. obsd.	220	231	235	239

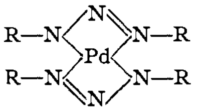
Discussion

Apart from the novelty of the four-membered ring involved in the chelate formulation of triazene metallic complexes, an interesting case of resonance also arises. In the triazenes themselves, in the monomeric form, resonance cannot occur but tautomerism probably does, and is the usual explanation offered for the failure to detect isomerism in unsymmetrical triazenes. The double bond–single bond nitrogen angle is probably very close to the normal angle of 125° and the group could thus chelate with suitable metals. The resulting metallic complexes then satisfy all of the conditions for resonance[6] which may occur between the two structures. That resonance does occur in these metallic complexes is evidenced by their marked stability, particularly of the palladous and cuprous complexes, and by the failure to detect isomerism in the silver and mercury salts of such unsymmetrical triazenes as 3-nitrodiazoaminobenzene.[7]



The unstable tris-diazoaminobenzenepalladium (I) and the corresponding dimethyl compound (V) as far as can be ascertained from a survey of the literature are the first hexacovalent bivalent palladous compounds described. Although the palladous ion is only ten electrons short of the xenon structure, twelve electrons must be contributed in such an arrangement. A similar excess of two electrons occurs, however, in hexacovalent nickelous complexes. The triazene groups in these compounds are probably arranged octahedrally about the metallic atom in *cis* positions. The compounds are apparently coördinately saturated, but substitution of the unique triazene molecule (with the imino hydrogen still intact) is easily achieved. Since substitution may yield a mono-ethylenediamine complex (III) or a bis-pyridine derivative (II), the unique triazene group must occupy two coördination positions.

The palladium bis compounds IV, VI are considered as typical tetracovalent square coördinated complexes of the structure



$R = C_6H_5$ or C_7H_7

The striking stability of these compounds, which are unaffected by boiling concentrated hydrochloric acid, or caustic alkalies, and decompose above 300°, contrasts sharply with that of the parent triazenes, which are decomposed by cold dilute acids, and explode about 130°, and must be attributed to the resonating chelate rings. Although monomeric, at high concentrations in benzene there is some evidence of association as is indicated clearly by the molecular weight determinations on the more soluble compound (IV), which were carried out at almost double the concentration of (VI). The coördinate saturation of the compounds seems curious; but the inability of tetracovalent square coördinated nickelous and palladous compounds to pass to the hexacovalent complexes by reaction with ammonia, pyridine

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(4) P. Griess, *Ann.*, **137**, 53 (1866).

(5) Rast, *Ber.*, **54**, 1979 (1921).

(6) N. V. Sidgwick, *Chem. Soc. Ann. Reports*, **31**, 38 (1934).

(7) F. P. Dwyer, *J. Australian Chem. Inst.*, **6**, 349 (1939).

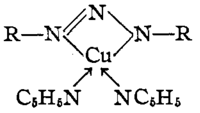
or ethylenediamine appears to be a very general phenomenon.

Bis-diazoaminobenzenecopper (VII) is probably constituted in a manner similar to the palladium compounds. The lower stability of the compounds may be attributed to well known sensitivity of diazo compounds toward copper metal or its salts. By reaction with pyridine or ethylenediamine a bis-pyridine compound (VIII) or a mono-ethylenediamine compound (IX) is formed. Although these substances may be constituted as hexacovalent complexes, in view of the comparative rarity of bivalent copper compounds with this higher coördination number[8] it seems more likely that the chelate ring is broken and the metal remains tetracovalent. The observation that the reaction does not occur at low temperatures offers some support for this contention.

The monomeric argentous compounds (XII), (XIII) which fail to react with strong coördinating groups must be considered as coördinately saturated and of the structure

$R = C_6H_5$ or C_7H_7

A similar structure is assigned to the remarkably stable cuprous compound (XI); but the coördination number is raised to the usual maximum of four in the bis-pyridine complex (X).



The slight association of the triazenes in benzene solution has led to the suggestion[9] that a dimeric form constituted in the manner of the carboxylic acids accounts for the "virtual" isomerism exhibited by the unsymmetrical triazenes. With the highly purified triazenes used in this research a similar slight association was noted. Since the effect is small compared with the pronounced dimerism of the substances, usually considered as associated, and only noticeable in very concentrated solutions, the evidence does not seem sufficient to support the suggestion. The structure proposed for the dimeric form has also been criticized on dipole measurements.[10]

Summary

Coördination experiments and molecular weight determinations show that the metallic salts of diazoamino compounds must be formulated as internal complexes in which the triazene group acts as a chelate group.

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(8) N. V. Sidgwick, "The Covalent Link in Chemistry," 1933, p. 202; W. Wardlaw, "Chem. Soc. Ann. Reports," 1933, p. 100.

(9) L. Hunter, *J. Chem. Soc.*, 320 (1937).

(10) R. W. Le Fèvre, *ibid.*, 1805 (1937).

SYDNEY, AUSTRALIA RECEIVED JUNE 13, 1940

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, TECHNICAL COLLEGE, AND UNIVERSITY, SYDNEY, AUSTRALIA]

The Diamagnetism of Nickel Triazene Complexes

BY F. P. DWYER AND D. P. MELLOR

There is evidence from quantum mechanical considerations,[1] X-ray crystal structure investigations,[2] studies of isomerism[3] and crystal optics[4] that complexes of nickel can be assigned to the tetrahedral-ionic or square-coördinated class on the basis of magnetic susceptibility measurements. Whenever any of the three physical lines of evidence has indicated the existence of square coördination, magnetic measurements have shown the compound to be diamagnetic.

In order to provide a physical test for the suggestion put forward in previous papers[5] that the triazenes can yield internal metallic complexes in which the —N=N—NH— group functions as a chelate group, several of the nickel complexes have now been prepared and investigated magnetically. The nickel compounds were chosen for this purpose since, of all the metallic complexes so far studied, those of nickel lend themselves most usefully to magnetic investigation. No distinction can be made magnetically between tetrahedral ionic and square coördinated complexes of Cu^{II}, Pt^{II} and Pd^{II}.

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(1) L. Pauling, THIS JOURNAL, **53**, 1367 (1931).

(2) E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, 459, 1475 (1935).

(3) S. Sugden, *ibid.*, 246 (1932).

(4) D. P. Mellor and F. M. Quodling, *J. Proc. Roy. Soc. N. S. Wales*, **70**, 205 (1936).

(5) F. P. Dwyer, *J. Australian Chem. Inst.*, **6**, 349, 362 (1939); THIS JOURNAL, **62**, 781 (1940).