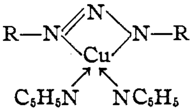
or ethylenediamine appears to be a very general phenomenon.

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.

[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).

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[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}.

[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).

Both *bis*-diazoaminobenzenenickel and *bis*-4,4'-dimethyldiazoaminobenzenenickel proved to be diamagnetic, and the only feasible way of formulating these compounds as square coördinated complexes seems to be that in which the triazene group is made to function as a chelate group.

Experimental

Pure[6] diazoaminobenzene (m. p. 100°), and 4,4'-dimethyldiazoaminobenzene were used in all of the preparations.

***Bis*-pyridine *bis*-Diazoaminobenzenenickel** (I).—Pure nickel acetate, 4.24 g., was dissolved in water (10 ml.) and pyridine (50 ml.) added gradually; diazoaminobenzene (8.0 g.) was stirred in, followed by methanol (80 ml.). The mixture was heated to 80° and 20 ml. of caustic soda solution 2 *N* added with stirring. On cooling brownish-yellow twinned leaflets were deposited. The compound was insoluble in benzene, but could be crystallized from pyridine or an acetone–pyridine mixture. In the absence of pyridine in acetone solution the compound was hydrolyzed by even traces of water.

Anal. Calcd. for $(C_{12}H_{10}N_3)_2Ni \cdot 2C_5H_5N$: Ni, 9.64. Found: Ni, 9.63.

***Bis*-diazoaminobenzenenickel** (II).—This compound was prepared from the *bis*-pyridine compound above by heating at 120–130° for ten to fifteen hours until pyridine was no longer evolved. The dark reddish-brown residue was extracted with boiling benzene and traces of the unchanged pyridine compound filtered off. Addition of alcohol to the benzene solution precipitated dark wine-red strongly pleochroic needles, which were purified by a number of crystallizations and finally dried at 100° for some hours. The compound was easily soluble in most organic solvents but not in alcohol or acetone. It melted at 278° and exploded at 285°. It was dissolved only very slowly by boiling concentrated hydrochloric acid, but was quite unaffected by boiling alkali or potassium cyanide solutions. The compound dissolved easily in hot pyridine to a red solution and crystallized unchanged on cooling; but by keeping the solution at 100° for some hours the original *bis*-pyridine compound (I) could be obtained. This by treatment with alcoholic potassium cyanide regenerated the original triazene (m. p. 100°).

Anal. Calcd. for $(C_{12}H_{10}N_3)_2Ni$: Ni, 13.03; mol. wt., 450. Found: Ni, 12.96; mol. wt., in benzene, ebullioscopic, 660, 643; cryoscopic, 952, 940.

Mono-ethylenediamine *bis*-Diazoaminobenzenenickel.—*Bis*-diazoaminobenzenenickel (II) failed to react with anhydrous ethylenediamine in cold benzene solution; but if molecular proportions of the substances were refluxed for two to three hours the color of the solution changed to yellow and the ethylenediamine derivative was precipitated by the addition of petroleum ether. Crystallized from benzene it gave yellowish-brown cruciform needles, containing one molecule of benzene of crystallization, which was lost at 100°, and melting at 148°.

Anal. Calcd. for $(C_{12}H_{10}N_3)_2Ni \cdot C_2H_8N_2$: Ni, 11.49. Found: Ni, 11.35.

***Bis*-4,4'-dimethyldiazoaminobenzenenickel** (III).—The *bis*-pyridine derivative prepared as before gave brownish-yellow plates insoluble in benzene.

Anal. Calcd. for $(C_{14}H_{14}N_3)_2Ni \cdot 2C_5H_5N$: Ni, 8.83. Found: Ni, 8.80.

Elimination of the pyridine as before at 120–130° gave a dense brown residue, which was dissolved in hot benzene and precipitated with alcohol. *Bis*-4,4'-dimethyldiazoaminobenzenenickel crystallized in wine-red pleochroic plates which exploded at 200° without melting. It was somewhat more soluble in organic solvents than the nickel compound (II) but showed a similar stability toward acids and alkalies. The diazoamino compound recovered as before melted at 119°.

Anal. Calcd. for $(C_{14}H_{14}N_3)_2Ni$: Ni, 11.58; mol. wt., 506. Found: Ni, 11.45; mol. wt. in benzene, ebullioscopic, 1023, 954, 868, 622; (mol. wt. 868 and 622 are at same concentration as mol. wt. 954, but at the end of one hour and one and one-half hours, respectively); cryoscopic, 1082, 1007.

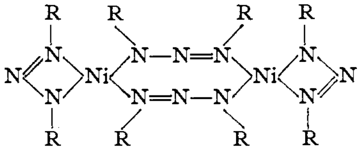
Reaction with Pyridine and Ethylenediamine.—The nickel compound (III) could be crystallized from hot pyridine without any coördination by the solvent, but, as before, gave the *bis*-pyridine compound by long heating. Similarly, it was not affected in the cold in benzene solution by even a large excess of anhydrous ethylenediamine. By refluxing with ethylenediamine (1 mole) for several hours it was transformed into the yellow mono-ethylenediamine derivative, m. p. 140°. The same substance was obtained at room temperature from the *bis*-pyridine derivative and ethylenediamine (1 mole).

Anal. Calcd. for $(C_{14}H_{14}N_3)_2Ni \cdot C_2H_8N_2$: Ni, 10.36. Found: Ni, 10.37.

Magnetic Measurements.—Susceptibility measurements were made by the Gouy method. *Bis*-diazoaminobenzenenickel (II) was diamagnetic: $\psi = -0.31 \times 10^{-6}$; *bis*-4,4'-dimethyldiazoaminobenzenenickel (III) was diamagnetic: $\psi = -0.29 \times 10^{-6}$; *bis*-pyridine *bis*-4,4'-dimethyldiazoaminobenzenenickel was paramagnetic: $\psi = +6.24 \times 10^{-6}$, $\psi_M = 4150 \times 10^{-6}$ ($T = 289°$ A.). Allowing for the diamagnetism of the chelated groups, and assuming the validity of Curie's law, the magnetic moment of the nickel in the latter compound is 3.38 Bohr magnetons. There are thus two unpaired electrons in the nickel atom.

Discussion

The most interesting feature that arises from molecular weight determinations of the two deep red diamagnetic complexes is their pronounced dimerism. From a consideration of their diamagnetism, their remarkable stability and their indifference toward powerful coördinating groups the following structure is proposed for I and II



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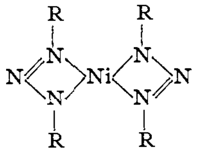
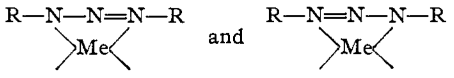
(6) F. P. Dwyer, *J. Soc. Chem. Ind.*, **56**, 70 (1937).

In boiling benzene the molecular weight determinations show a gradual breakdown of the dimeric molecule into



On cooling the equilibrium is shifted to favor the dimeric form.

If the 125° double bond–single bond angle is assumed for trivalent nitrogen, and the usual assumption is made that the Ni–N bond distances are equal to the sum of the covalent radii, it can be shown by scale diagrams that the nickel bonds in either of the above structures are very nearly at 90°. Chelation should occur very readily, and resonance then becomes possible between the structures



Such resonance must make a considerable contribution to the stability of the complex.

The four-membered ring structures proposed are not unique. Thus nickel ethylxanthogenate ($Ni(C_2H_5OCS_2)_2$) and nickel ethyldithiocarbamate ($Ni(C_2H_5NHCS_2)_2$) are diamagnetic[7] and hence square coördinated, both structures involving a four-membered ring. The eight-membered ring involved in bridging the nickel atoms, however, is very unusual. There is evidence for its occurrence in the *bis*-ethylenediamine cobalt complexes with sulfonyldiacetic acid[8] and with homophthalic acid.[9]

The parent *bis*-pyridine derivatives presumably have an octahedral structure with the pyridine molecules occupying *cis* positions, since they can be replaced at room temperature by one molecule of ethylenediamine. Although the transformation involves a spatial rearrangement of the triazene groups around the metallic atom, the *bis*-pyridine derivatives are easily changed into II and III, whilst the addition of the pyridine molecules which could occur in 1,6 positions without any rearrangement of the triazene groups is much more difficult.

This appears to be a fairly general phenomenon with diamagnetic nickel complexes, and has already been referred to with palladous complexes.[5] It is not possible for instance to coordinate pyridine or ammonia molecules to the diamagnetic nickel glyoxime complexes, while on the other hand a *bis*-pyridine derivative is readily prepared from the paramagnetic *bis*-acetonylacetonenickel.

Summary

Magnetic susceptibility measurements show that nickel complexes of diazoaminobenzene and 4,4′-dimethyldiazoaminobenzene are diamagnetic and hence contain square coördinated nickel atoms. The only feasible formulation of these compounds as square coördinated complexes seems to be that in which the triazene group is made to function as a chelate group.

SYDNEY, AUSTRALIA

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[8] T. S. Price and S. A. Brazier, *J. Chem. Soc.*, **107**, 1367 (1915).

[9] J. C. Duff, *ibid.*, **119**, 1982 (1921).