423. *The Structure of Some Di-(3-methyl-1,5-diarylformazyl)-nickel*(II) *Complexes.*

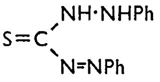
By H. Irving, J. B. Gill, and (in part) W. R. Cross.

3-Methyl-1,5-diphenyl-, 3-methyl-1(or 5)-phenyl-5(or 1)-*p*-tolyl-, and 3-methyl-1,5-di-*p*-tolyl-formazan have been prepared and their absorption spectra in benzene and pyridine studied. The formazans yield diamagnetic bis-complexes with nickel(II) [but not with Hg(II) or Zn] which are monomeric in benzene and form loose pyridine adducts having characteristic spectra.

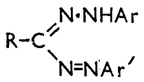
Di-[3-methyl-1(or 5)-phenyl-5(or 1)-*p*-tolylformazyl]nickel(II) has been resolved by chromatography on (+)-quartz, but complexes with the 1,5-diphenyl and the 1,5-di-*p*-tolyl analogue were not resolvable. It is concluded that these nickel complexes contain six-membered chelate rings with either distorted planar or grossly distorted tetrahedral configurations of nitrogen atoms round the central metal. The significance of these results in interpreting the structure of metal–dithizone complexes is discussed.

1,5-Diphenylformazan has been shown to form a monohydrate. Like 1,3,5-triphenylformazan it forms complexes with nickel, cobalt, and copper, but only gives a loose adduct with mercuric chloride. 1-Methyl-1,3,5-triphenylformazan could not be prepared by coupling a diazonium solution with benzaldehyde methylphenylhydrazone, or by the methylation of 1,3,5-triphenylformazan.

Although the empirical formulæ of most metal complexes of the analytical reagent dithizone (diphenylthiocarbazone) (I) and 3-mercapto-1,5-diphenylformazan (II; R = SH, Ar = Ar′ = Ph) have been established, their structure still remains in doubt. Following Fischer,[1] most authors formulate the so-called keto-complexes as derivatives of the tautomeric form (I), the imino-hydrogen atom being replaced by metal. Since metals which most readily form dithizonates (*i.e.*, Ag, Hg, Cu, Co, Ni, Cd, Tl, Bi, Zn, In) are precisely those which are most readily separated as sulphides in qualitative analysis it seems rather more probable that their dithizone complexes would contain metal–sulphur bonds and that they could be derived formally from the thiol tautomer of dithizone (II; R = SH, Ar = Ar′ = Ph). This suggestion [2] is supported by the failure of *S*-methyldithizone (II; R = SMe, Ar = Ar′ = Ph) to form metal complexes [3] under conditions where dithizone reacts readily, and more decisively by the results of an *X*-ray crystallographic study of mercury dithizonate [4] which establishes unambiguously the presence of the grouping >C–S–Hg–S–C<.



(I)



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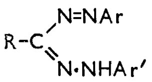

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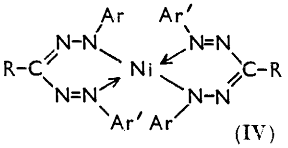

(IV)

A further argument against Fischer's formulation with metal–nitrogen bonds can be based on steric considerations. Examination of models shows that steric hindrance to co-ordination due to the proximity of the four bulky phenyl groups would be least with metals such as mercury, zinc, and cadmium which favour tetrahedral bond orbitals, but would be so large as to inhibit complex formation completely with metals such as copper and nickel which adopt square-planar configurations in their inner chelate complexes (unless gross distortion from coplanarity could occur). In fact there appears to be no great difference between the ease of formation of dithizone complexes with these different

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[1] Fischer, *Angew. Chem.*, 1934, **47**, 685; 1937, **50**, 919.

[2] Irving, Cooke, Woodger, and Williams, *J.*, 1949, 1847.

[3] Irving and Bell, *Nature*, 1952, **169**, 756; *J.*, 1954, 4253.

[4] Harding, *J.*, 1958, 4136.

metals, and the absorption spectra of the corresponding complexes present no distinguishing features. That dinaphthylthiocarbazone forms metal complexes as readily as dithizone, despite the enormously increased steric hindrance to co-ordination that would result if imino-hydrogen atoms were involved, appears to be a cogent argument against Fischer's views.

Nevertheless it has been established that complex formation can involve the imino-hydrogen of a formazan (at least when no alternative is available), for Hunter and Roberts [5] prepared copper, cobalt, and nickel complexes of diphenyl-, phenyl-*p*-tolyl-, *p*-methoxyphenyl-phenyl- and *p*-bromophenyl-phenyl-formazan, and nickel and cobaltous complexes with β- and α-naphthylphenylformazan (II; R = H). Many further examples are provided by the work of Wizinger and his collaborators.[6] Since a coplanar arrangement of nitrogen–metal bonds appears to be sterically impossible, at least for nickel and copper complexes of diarylformazans, it was decided to re-examine such substances to see what light they might throw on the structure of metal dithizonates and, more particularly, whether the nickel complexes would be forced to adopt a tetrahedral disposition of bonds and thus provide unambiguous examples of paramagnetic four-covalent complexes.

The preparation of pure substituted formazans is notoriously difficult, for small changes in reaction conditions readily lead to mixtures of different products.[7] These preparative difficulties and the additional possibility of polymorphism led originally to the belief that pairs of isomers (II and III) could be obtained by the action of the diazonium salt $Ar'\cdot N_2^+X^-$ upon an arylhydrazone Ar·NH·N:CHR, or by the action of $Ar\cdot N_2^+X^-$ upon Ar'·NH·N:CHR respectively. Hunter and Roberts were the first to prove the identity of a number of alleged isomer pairs by mixed melting points [8] and by their yielding identical metal derivatives.[5,8] Kuhn and Jerchel [9] prepared other possible isomeric pairs and established the identity of their absorption spectra and *X*-ray powder diagams, and Ragno and Bruno [10] showed that a number of possible isomeric pairs gave the same products on reduction and yielded the same sodium and potassium salts. With the exception of an unconfirmed claim by Ragno and Oreste [11] of certain differences in the pair (II and III; R = Me, Ar = *p*-nitrophenyl, Ar' = 2,4-dinitrophenyl), the absence of isomerism in unsymetrically substituted 1,5-diarylformazans may be taken as proof of mesomerism (II $\longleftrightarrow$ III) brought about by internal hydrogen bonding.[8] There remains, however, the possibility of *cis–trans*-isomerism about the –N:N– bonds, and *syn–anti*-isomerism about the :C=N– bonds, leading to four possible geometrical isomers. This problem has been thoroughly studied by Kuhn and his collaborators [12,13] who have demonstrated the effect of light and the nature of the solvent upon the equilibria between the various forms in solution.

The absence of isomers of copper, nickel, or cobaltous complexes of unsymmetrical 1,5-diarylformazans [5,8] implies mesomerism in the chelate ring system (one canonical form of the nickel complex is shown as IV) with identity of bond order in the pairs of carbon–nitrogen, nitrogen–nitrogen, and nitrogen–metal bonds. Resonance will thus stabilise the chelate rings in a planar conformation and, if the nickel were in square-planar co-ordination, cause the aryl groups to overlap. Although this steric factor appears to favour the formation of complexes with metals which adopt a tetrahedral disposition of bonds we have not succeeded in preparing a mercury or zinc complex from any of a number of diarylformazans (*e.g.*, II; R = H, alkyl, or aryl). This is in striking contrast to the ease with

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[5] Hunter and Roberts, *J.*, 1941, 823.

[6] Wizinger, *Z. Naturforsch.*, 1954, **11**, 729 and refs. therein; cf. Seyhan and Fernelius, *Chem. Ber.*, 1956, **89**, 2482 and refs. therein.

[7] Hauptmann and Perisse, *Chem. Ber.*, 1956, **89**, 1081.

[8] Hunter and Roberts, *J.*, 1941, 820.

[9] Kuhn and Jerchel, *Ber.*, 1941, **74**, 941.

[10] Ragno and Bruno, *Gazzetta*, 1946, **76**, 485.

[11] Ragno and Oreste, *Gazzetta*, 1948, **78**, 228.

[12] Hausser, Jerchel, and Kuhn, *Chem. Ber.*, 1949, **82**, 515.

[13] Kuhn and Weitz, *Chem. Ber.*, 1953, **86**, 1199.

which mercury and zinc complexes of dithizone are formed and is an argument against Fischer's formulation (see above).

In preliminary studies we confirmed Hunter and Roberts's preparation of cobalt, nickel, and copper complexes of 1,3,5-triphenylformazan,[5] and extended their method to other formazans. In general, the metal content of the copper complexes was higher than that calculated for a simple dichelated complex and would not be correct for any reasonable hydroxy-bridged structure. It appears that the method of preparation does not allow complete removal of basic copper salts from the very sparingly soluble complexes.[5] On the other hand, nickel complexes of 3-alkyl(or aryl)-1,5-diarylformazans were obtained pure and in excellent yield by the interaction of their components in absolute alcohol even when poor yields resulted by Hunter and Roberts's procedure.[5] The nickel complex of 1,5-diphenylformazan was obtained pure, but in poor yield. In this connection we observed that the crystalline red parent formazan of m. p. 117° gave a slightly lighter coloured monohydrate of m. p. 84—85° when recrystallised from aqueous methanol. This, and not a change in the proportions of geometrical isomers (cf. ref. 12), probably explains why Ponzio and Gastaldi's preparation,[14] which had been recrystallised from aqueous alcohol, was reported as melting between 100° and 108°.

FIG. 1. *Absorption spectra of* 3-*methyl*-1(*or* 5)-*phenyl*-5(*or* 1)-p-*tolylformazan in* (*A*) *benzene and* (*B*) *in pyridine.*

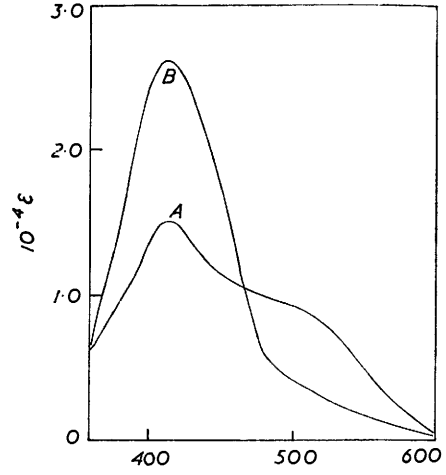
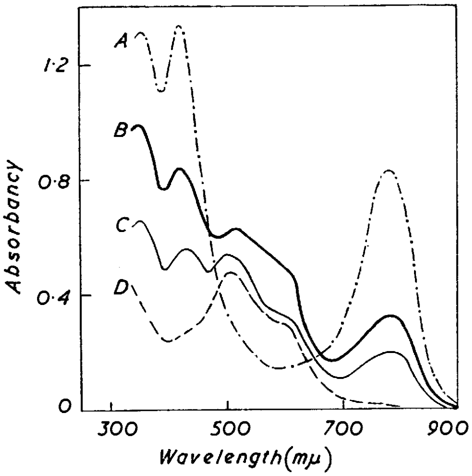


FIG. 2. *Effect of pyridine upon the absorption spectrum of a nickel–formazan complex in benzene.*



A, 9·091 × 10^{-5}M-*Solution of di*-[3-*methyl*-1(*or* 5)-*phenyl*-5(*or* 1)-p-*tolylformazyl*]*nickel*(II). *B*, *Spectrum* 2 *hours after addition of pyridine. C*, *Spectrum* 2 *days after addition of pyridine. D*, *Calculated spectrum of the adduct.*

3-Methyl-1,5-diphenyl-, 3-methyl-1(or 5)-phenyl-5(or 1)-*p*-tolyl-, and 3-methyl-1,5-di-*p*-tolyl-formazan were prepared by conventional methods [10,15] as finely crystalline red needles with a light blue reflex. Their absorption spectra in benzene (cf. Fig. 1) are very similar, with a well-defined peak which is progressively displaced towards longer wavelengths by the introduction of the *p*-methyl group [408 (ε 14,600), 413 (ε 14,500), and 420 mμ (ε 15,000) respectively]; Pupko and Pel'kis [16] have noted a similar effect in substituted dithizones. The similarity of the absorption spectrum of phenyl-*p*-tolylformazan to those of the diphenyl and ditolyl analogues, together with its intermediate position, provide further evidence for mesomerism (II $\longleftrightarrow$ III) in the formazan ring system.

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[14] Ponzio and Gastaldi, *Gazzetta*, 1914, **44**, 257.

[15] Bamberger and Pemsel, *Ber.*, 1902, **36**, 54, 87.

[16] Pupko and Pel'kis, *Zhur. obshchei Khim.*, 1954, **24**, 1640.

The presence of a shoulder in the absorption spectra of each formazan at about 480 mμ (ε 9300—10,300) indicates the presence of a second absorbing component and suggests that these benzene solutions are equilibrium mixtures of " red " and " yellow " geometric isomers such as have actually been isolated in the case of 1,3,5-triphenyl- and 3-ethyl-1,5-diphenyl-formazan.[12] An analysis of the absorption curves on this basis leads to the results of Table 1 which more clearly demonstrates the progressive effect of introducing the *p*-methyl groups.

TABLE 1. *Absorption spectra of* 3-*methyl*-1,5-*diarylformazans* (II; R = Me) *in benzene.*

Ar	Ar′	Concn. (10^{-5}M)	" Yellow " isomer $\lambda_{max.}$	ε	" Red " isomer $\lambda_{max.}$	ε
Ph	Ph	8·100	406	14,000	498	8,600
Ph	*p*-Tolyl	8·000	412	14,400	508	8,750
p-Tolyl	*p*-Tolyl	10·62	418	15,000	516	9,200

The absorption spectrum of a solution of the unsymmetrical 3-methylformazan (II or III; R = Me, Ar = Ph, Ar′ = *p*-tolyl) in pyridine still shows evidence of the presence of some of the " red " isomer, though in much lower proportion: the positions of the maxima (415 and 512 mμ) are scarcely changed. Since they are obtained by dividing measured absorbancies by the total weight of solute, the " molecular extinction coefficients " given in Table 1 are considerably underestimated. On the assumption that the molecular extinction coefficient is substantially the same for solutions in benzene and pyridine and that solutions in either solvent consist of an equilibrium mixture of the same two isomers, each of which has a single peak in its absorption spectrum, it can be shown that the " red " isomer absorbing at 512 mμ will have a molecular extinction coefficient of 13,300 while that of the " yellow " isomer would be 33,500 at 415 mμ. The benzene solution then contains 55% of " red " and 45% of " yellow " isomer while the pyridine solution contains 80% of the former. It is noteworthy that Hausser, Jerchel, and Kuhn,[12] who isolated the individual isomers of 3-ethyl-1,5-diphenylformazan report that, immediately after dissolution in benzene, the " yellow " form gave a spectrum with a main band at 405 mμ (ε 69,000) with a subsidiary peak (due probably to some of the " red " form) at 480 mμ (ε 5000): the red form gave peaks at 480 (ε 31,000) and 405 mμ (ε 11,000) corresponding closely to the equilibrium mixture.

Nickel complexes of all three formazans were obtained pure and in high yield as well crystallised black solids which were stable up to 250° but melted with decomposition. They are slightly soluble in benzene and even less so in n-hexane, to give yellow-brown solutions. They are insoluble in all other common solvents, except pyridine in which they dissolve to the extent of about 1·5 g./l. Their absorption spectra in benzene (cf. Fig. 2; Table 2) are very similar, for they exhibit two prominent peaks at 357—360 and 418—424 mμ with a well-defined maximum in the near-infrared region. By using n-hexane as solvent it was possible to record the spectrum of di-(3-methyl-1-phenyl-5-*p*-tolylformazyl)-nickel(II) into the near-ultraviolet region (Table 2).

TABLE 2. *The absorption spectra of nickel complexes of* 3-*methyl*-1,5-*diaryl-formazans* (II; R = Me).

Ar	Ar′	Concn. (10^{-5}M)	$\lambda_{max.}$*	$\lambda_{min.}$	$\lambda_{max.}$	$\lambda_{min.}$	$\lambda_{max.}$
Ph	Ph	7·782	357 (13,300)	383 (12,100)	418 (14,800)	600 (1550)	780 (9200)
Ph	*p*-Tolyl	9·091	360 (14,400)	389 (12,200)	420 (14,600)	600 (1650)	785 (9070)
Ph	*p*-Tolyl †	2·750	360 (15,600)	386 (13,100)	418 (15,600)	—	780 (9750)
p-Tolyl	*p*-Tolyl	7·416	360 (14,700)	393 (12,300)	420 (14,900)	600 (1900)	785 (9240)

* Figures in parentheses are molecular extinction coefficients.

† Measured in n-hexane. Additional features in this solvent were: λ 225 (sh) (28,000); $\lambda_{min.}$ 247 (23,600); $\lambda_{max.}$ 260 (25,820); $\lambda_{min.}$ 290 (15,600); $\lambda_{max.}$ 307 (18,600); $\lambda_{min.}$ 339 mμ (14,200).

The strong band at ~420 mμ is characteristic of a covalent nickel chelate complex[17]

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[17] Sacconi, Paoletti, and del Re, *J. Amer. Chem. Soc.*, 1957, **79**, 4062.

and its intensity (log ε 4·1) is that of an allowed transition, probably $3d \longrightarrow 4s$. From a study of the absorption spectra of a number of quadricovalent nickel(II) complexes Sacconi, Paoletti, and Maggio [18] concluded that " a band at 406—410 mμ can be recognised as that of nickel chelates with dsp^2-covalent structure." This deduction was confirmed in the present instance by measurements of the magnetic susceptibilities of the three nickel complexes as solids. They all proved to be diamagnetic ($10^6\chi = -0{\cdot}5$ to $-0{\cdot}8$ c.g.s. unit/g.). With azobenzene as a reference solute it was possible by an isopiestic method [19] to show that the nickel complexes of 1,3,5-triphenylformazan, 3-methyl-1,5-diphenylformazan, and 3-methyl-1-phenyl-5-*p*-tolylformazan were monomeric in benzene solution.

These results show that these nickel–formazan complexes are spin-paired compounds, presumably with dsp^2-bonding, and that their alternative formulation as spin-free complexes with sp^3-hybrid bonds in tetrahedral disposition must be rejected. Further evidence in favour of planar as opposed to tetrahedral bonding was sought by treating the compounds with pyridine which in the former, but not in the latter case, should give a paramagnetic 6-co-ordinate adduct.[20] When 1 ml. of pure pyridine (a factitious excess) was added to 25 ml. of a solution of the nickel complex (IV; R = Me, Ar = Ar′ = Ph) (0·0637 g./l.) absorption peaks at 357, 418, and 780 mμ (see Fig. 2, curve *A*) due to the original nickel–formazan complex were lowered, while new bands appeared between 500 and 700 mμ. The absorption spectra after 2 hours and 2 days respectively are shown in Fig. 2, curves *B* and *C*. By using the optical absorption at 780 mμ the course of the reaction with time could be followed. It was rapid at first, but not complete after 1 day even when a great excess of pyridine was used. The residual absorption at 780 mμ clearly corresponded to unchanged nickel–formazan complex, for the values of the absorbancies at all wavelengths between 700 and 900 mμ were in a constant ratio (0·589) to those of the original nickel complex in this range. Independent measurements had shown that Beer's law was obeyed by the parent complex over the concentration range from 0 to $1{\cdot}1 \times 10^{-4}$M, both at 418 and 780 mμ. Since it had already been shown (Fig. 1) that the formazan itself did not form a complex with pyridine it was legitimate to substract the contribution of unchanged nickel–formazan complex from curve *C* and so arrive at that of the adduct alone (curve *D*). This proved to be very much like that of the original formazan, with one, rather weak, main band at 510 mμ (ε 5070) with a shoulder at 595 mμ. Similar experiments with di-(3-methyl-1,5-diphenylformazyl)nickel(II) and pyridine disclosed a similar adduct, giving an absorption maximum at 505 mμ (ε 4820) and a shoulder at 595 mμ. Attempts to prepare the pyridine adducts in the solid state failed. The black crystals which separated from a solution of di-(3-methyl-1,5-diphenylformazyl)nickel(II) in hot pyridine gave an absorption spectrum in benzene identical with that of the original metal complex, and they lost no weight when placed *in vacuo* over sulphuric acid for 3 days. We have not yet investigated the magnetic properties of the solutions of the nickel–formazan complexes; and since these complexes decompose on melting, it is impossible to state whether, as with di-(*N*-alkylsalicylaldimine)nickel(II) complexes,[21] diamagnetism is confined to the solid state.

The reflectance spectra of the three nickel–formazan complexes were very similar. The most prominent feature for di-(3-methyl-1,5-diphenylformazyl)nickel(II) was a fairly sharp absorption band centred at 386 mμ, which was displaced successively to 389 and 410 mμ by introduction of *p*-methyl groups. All three complexes had a broad band centred at 705—720 mμ.

The diamagnetism and spectral data for these 4-co-ordinate nickel–formazan complexes, and their reluctance to form stable adducts with pyridine, are consistent with either

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[18] Sacconi, Paoletti, and Maggio, *J. Amer. Chem. Soc.*, 1957, **79**, 4067. Among other earlier papers in this field see McKenzie, Mellor, Mills, and Short, *J. Proc. Roy. Soc. New S. Wales*, 1944, **78**, 70.

[19] Morton, Campbell, and Ma, *Analyst*, 1953, **78**, 722.

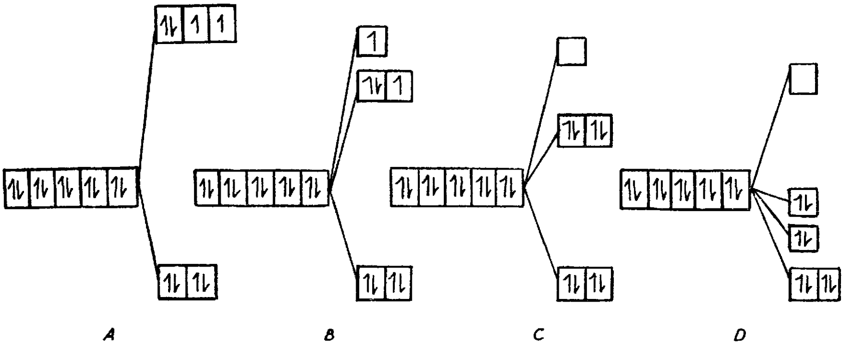
[20] Basolo and Matoush, *J. Amer. Chem. Soc.*, 1953, **75**, 5663.

[21] Sacconi, Cini, and Maggio, *J. Amer. Chem. Soc.*, 1957, **79**, 3933.

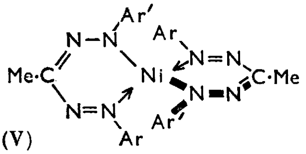
a slightly distorted planar structure or a sufficiently distorted tetrahedral structure. For, while ligand-field theory predicts paramagnetism for a Ni(II) complex with eight *d*-electrons in a regular tetrahedral field, and diamagnetism in a square planar field (Fig. 3, schemes *A* and *D*), a Jahn–Teller distortion of the tetrahedron comprising a compression along a two-fold axis of symmetry would cause the upper triplet of *A* to split into an upper singlet and a lower doublet (Fig. 3, *B*). If the distortion were large enough and the energy separation of the two uppermost levels great enough (Fig. 3, *C*), diamagnetism would result.

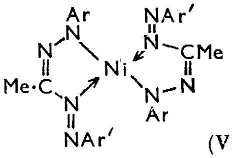
Evidence for the non-coplanarity of the chelate rings in di-(3-methyl-1-phenyl-5-*p*-tolylformazyl)nickel(II) (V; R = Me, Ar = phenyl, Ar′ = *p*-tolyl) was obtained by partial resolution on a column of (+)-quartz. The most active fractions had $[M]_D^{22}$ +49·3° and —45·0° respectively and racemised only slowly at room temperature. The complex can therefore be formulated as (V). The alternative formulation (VI) with 5-membered chelate rings is inconsistent with the absence of isomers when Ar and Ar′ are dissimilar (see above), and there would still be excessive steric hindrance to a planar disposition about the nickel atom in the *cis*-form, though less in the *trans*-form. If, in this case, steric strain were relieved by the adoption of a non-coplanar arrangement of Ni–N bonds, an asymmetric molecule would result whether or not the aryl groups were identical. However, no optical resolution of di-[3-methyl-1,5-diphenyl(or ditolyl)formazyl]nickel(II) could be achieved under conditions identical with those employed successfully for the unsymmetrical analogue (Ar = Ph, Ar′ = *p*-tolyl).

Fig. 3. *Splitting of energy levels in distorted planar or tetrahedral nickel complexes.*



The precise conformation of these nickel–formazan complexes must await a full *X*-ray crystallographic study. A coplanar arrangement of four Ni–N bonds can only be achieved if the formazan rings are severely buckled (with consequent loss of resonance stabilisation energy) and if the aryl groups from the two ligands lie in nearly parallel planes and in close proximity. This may explain why such compounds are only obtained readily with nickel and to a smaller extent with copper. It is less easy to see why no genuine tetrahedral


(V)


(VI)

complexes are formed with mercury, zinc, or cadmium. Their non-existence, the excessively low solubility of nickel and copper complexes in chloroform or carbon tetrachloride, and the evidence of their absorption spectra (which differs so completely from the simple spectra characteristic of metal–dithizone complexes) all point against Fischer's formulation [1] of dithizone complexes as compounds in which the imino-nitrogen atom has been replaced by a metal.

EXPERIMENTAL

Preparation of 3-*Methyl*-1,5-*diphenylformazan.*—After experience of Wedekind's procedure starting from pyruvic acid,[22] and that of Bamberger and Pemsel,[15] both of which gave poor yields and a high proportion of tarry by-products, the following preparation, based largely on the work of Ragno and Bruno [10] was found to give the most reproducible results.

Acetaldehyde phenylhydrazone (10 g.; m. p. 92°; freshly recrystallised from ethanol) was dissolved in warm ethanol (50 ml.), and the solution was cooled to 0°. Over a period of 5 min. a diazonium solution prepared at 0° from aniline (12 g.), concentrated hydrochloric acid (27 ml.), water (50 ml.), and sodium nitrite (9 g.) was added. After a further 2 hours' stirring, a red oil separated which solidified overnight at 0°. The total yield from five such preparations (76·5 g.) was collected and dried *in vacuo* over calcium chloride. After one recrystallisation from ethanol, orange-red needles, m. p. 121°, were obtained (49 g., 59%). After two more recrystallisations the m. p. was constant at 125·5° (Found: N, 23·5. Calc. for $C_{14}H_{14}N_4$: N, 23·5%). Wedekind [22] reported 121°, Ragno and Bruno [10] 123°, and Hausser, Jerchel, and Kuhn [12] 124—126°.

3-*Methyl*-1,5-*di*-p-*tolylformazan* (23·1 g.), prepared similarly from acetaldehyde *p*-tolylhydrazone (15 g.; m. p. 96—97°), formed orange-red needles, m. p. 181—182°, with a light blue reflex, from boiling ethanol (Found: N, 21·2. $C_{16}H_{18}N_4$ requires N, 21·2%).

3-*Methyl*-1(*or* 5)-*phenyl*-5(*or* 1)-p-*tolylformazan* (15·5 g.), prepared similarly by coupling a solution of acetaldehyde phenylhydrazone (10 g.) with a diazonium solution prepared from *p*-toluidine (8 g.) at 0°, recrystallised from ethanol (charcoal) as orange-red needles with a light blue reflex, m. p. 155·5° (5·5 g., 30%) (Found: C, 71·8; H, 6·4; N, 22·3. $C_{15}H_{16}N_4$ requires C, 71·4; H, 6·4; N, 22·2%).

Preparation of Di-(3-*methyl*-1,5-*diphenylformazyl*)*nickel*(II).—A solution of the formazan (3·45 g.) in ethanol (50 ml.) was heated under reflux (1·5 hr.) with a solution of nickel acetate (1·85 g.) in ethanol (50 ml.). The solid product was collected and any adhering formazan was removed by washing with alcohol until the washings were colourless. The residue was then washed in turn with N-hydrochloric acid, water, and ethanol, and dried *in vacuo* ($CaCl_2$). The aqueous washings gave no test for nickel with dimethylglyoxime. *Di*-(3-*methyl*-1,5-*diphenylformazyl*)*nickel*(II) formed black flaky crystals with a strong metallic lustre (2·48 g., 95·7%), decomp. >300° without melting [Found: C, 63·0; H, 4·9; N, 21·0; Ni, 11·0%; *M*(isopiestic in benzene),[19] 502, 503. $C_{28}H_{26}N_8Ni$ requires C, 63·1; H, 4·9; N, 21·0; Ni, 11·0%; *M*, 533·3].

The solid complex is diamagnetic with $10^6\chi = -0{\cdot}8$ c.g.s. unit/g. Like the other nickel complexes described below it is only slightly soluble in benzene and very sparingly soluble in n-hexane in which it gives a yellow-brown solution. It is insoluble in all other common solvents except pyridine (~1·3 g./l.).

Di-(3-methyl-1,5-diphenylformazyl)copper(II), prepared similarly in 50% yield from the formazan and cupric acetate, formed an impure micro-crystalline powder (Found: Cu, 14·1. Calc. for $C_{28}H_{26}N_8Cu$: Cu, 11·8%).

Attempts to prepare cobalt and zinc complexes were unsuccessful and the formazan was recovered unchanged by diluting the reaction mixture with water.

Di-(3-*methyl*-1-*phenyl*-5-p-*tolylformazyl*)*nickel*(II) was obtained from the formazan in 65% yield as black crystals whose diamagnetic susceptibility was $10^6\chi = -0{\cdot}5$ c.g.s. unit/g. [Found: C, 64·4; H, 5·5; N, 19·9; Ni, 10·4%; *M* (isopiestic in benzene), 537, 537. $C_{30}H_{30}N_8Ni$ requires C, 64·2; H, 5·4; N, 20·0; Ni, 10·4%; *M*, 561·3]. No cobalt complex was formed when an alcoholic solution of the formazan was heated under reflux with cobaltous acetate. *Di*-(3-*methyl*-1,5-*di*-p-*tolylformazyl*)*nickel*(II), prepared similarly in 86% yield, formed flaky black crystals which decomp. >300° (Found: Ni, 10·2. $C_{32}H_{34}N_8Ni$ requires Ni, 10·0%).

Hydrate of 1,5-*Diphenylformazan.*—Preparation of 1,5-diphenylformazan by coupling

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[22] von Pechmann, *Ber.*, 1892, **25**, 3187; 1894, **27**, 2927.

malonic acid with benzenediazonium chloride [23] was found to depend upon reaction conditions. It was essential to keep the temperature below 3° and the pH above 9 during the coupling.[7]

To a diazonium solution prepared from aniline (23 g.), concentrated hydrochloric acid (82 ml.), water (100 ml.), and sodium nitrite (18 g.), was added sodium acetate (50 g.) in water (100 ml.). The whole was cooled to $-5°$ and added in 10 min. to a stirred solution (also at $-5°$) of malonic acid (26 g.) and hydrated sodium acetate (50 g.) in water (300 ml.). The temperature was not allowed to rise above 3° during the addition. After being stirred for a further 2 hr. the mixture was left in a freezing-mixture for 36 hr. The flocculent red product (42 g.; m. p. 90°) was collected and dried *in vacuo* ($CaCl_2$). After a further 5 days *in vacuo* over phosphoric oxide the solid had darkened and the m. p. rose to 113°. From dry methanol (charcoal) 1,5-diphenylformazan formed small dark red crystals with a faint violet lustre and m. p. 117° (Found: N, 25·0. Calc. for $C_{13}H_{12}N_4$: N, 25·1%). The m. p. depends somewhat on the rate of heating (cf. 116—119°, 117—120°, von Pechman [23]; 117—119°, Claisen [24]; 117°, Walther [25]; 120°, 100—108°, Ponzio and Gastaldi [14]; 116°, Busch and Beust [26]; and 114—116°, Hausser, Jerchel, and Kuhn [12]). When recrystallised from water–methanol (1 : 1·5) 1,5-diphenylformazan formed a dark red *monohydrate,* m. p. 84—85° which gradually lost water when heated *in vacuo* over phosphoric oxide and reverted to the anhydrous formazan of m. p. 117° (Loss at 64° 1 mm.: 7·1, 6·9. $C_{13}H_{12}N_4,H_2O$ requires H_2O, 7·4%).

Di-(1,5-*diphenylformazyl*)*nickel*(II) was obtained in fair yield as a black micro-crystalline powder (Found: Ni, 11·7. $C_{26}H_{22}N_8Ni$ requires Ni, 11·6%). The copper complex, prepared similarly, was not obtained pure (Found: Cu, 15·6. Calc. for $C_{26}H_{22}N_8Cu$: Cu, 12·4%).

D-(1,3,5-triphenylformazyl)nickel(II) was obtained in 91·5% yield from 1,3,5-triphenylformazan by Hunter and Roberts's method [8] as a black micro-crystalline powder, decomp. >300° [Found: Ni, 8·85%; *M* (isopiestic in benzene), 621, 627. Calc. for $C_{38}H_{30}N_8Ni$: Ni, 8·9%; *M*, 657·4], with $10^6\chi$ $-0·5$ c.g.s. unit/g.

Absorption Spectra.—These were measured with a Unicam S.P. 500 with a cell-compartment at 25° (thermostat) and matched cells.

Action of Pyridine on a Solution of Di-(3-*methyl-*1,5-*diphenylformazyl*)*nickel*(II) *in Benzene.*—Redistilled pyridine (1 ml.) was added to a solution (25 ml.; 0·0637 g./l.) of the nickel complex in benzene. A 1 cm. stoppered cell was filled with this mixture and the spectrum recorded after various times; a reference cell filled with a mixture of benzene (25 ml.) and pyridine (1 ml.) was used. Kinetic measurements at 780 mμ on (*a*) a solution containing 0·0612 g. of the nickel complex and 39·1 g. of pyridine (molar ratio 1 : 4300) per l. and (*b*) a solution containing 0·1126 g. of the nickel complex and 0·196 g. of pyridine (molar ratio 1 : 2·2) per l. gave the following results.

Time (min.)		0	20	40	60	100	200	500	1000
Optical density in 1 cm. cell	(*a*)	1·4	0·54	0·36	0·34	0·32	0·29	0·24	0·21
	(*b*)	2·0	1·36	1·20	1·17	1·16	1·14	1·13	1·12

Attempted Preparation of the Adduct of Pyridine and Di-(3-*methyl-*1,5-*diphenylformazyl*)-*nickel*(II).—A solution of the nickel complex (0·3 g.) in hot pyridine (15 ml.) was heated on a water-bath for 1 hr. The black crystals which separated on cooling were collected and dried rapidly between filter papers. The absorption spectrum in benzene was identical with that of the original nickel–formazan complex. The remainder (0·2294 g.) was kept *in vacuo* over sulphuric acid (wt. after 1, 2, and 3 days: 0·2281, 0·2283, and 0·2280 g. respectively), then analysed (Found: Ni, 10·8. Calc. for $C_{28}H_{26}N_8Ni,2C_6H_5N$: Ni, 8·2. Calc. for $C_{28}H_{26}N_8Ni$: Ni, 11·0%).

Optical Resolution of Di-(3-*methyl-*1-*phenyl-*5-p-*tolylformazyl*)*nickel*(II).—(+)-Quartz (120 mesh) was washed with water, acetone, and benzene, heated at 100° in a partial vacuum over phosphoric oxide, and then placed in dry benzene in a chromatographic column (20 × 2 cm.).

A solution of the nickel complex in benzene (0·0021 g./10 ml.) was placed at the top of the column and eluted with benzene (~3—4 ml./min.). Successive samples of 50 drops each were collected and diluted to 35 ml. The optical rotation was determined at 22° in a Bellingham and Stanley polarimeter with sodium light and a 40 cm. cell. The concentration of complex in

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[23] Wedekind, *Ber.*, 1897, **30**, 2998.
[24] Claisen, *Annalen*, 1895, **287**, 368.
[25] Walther, *J. prakt. Chem.*, 1896, **53**, 475.
[26] Busch and Beust, *Ber.*, 1925, **58**, 443.

each sample was determined from the optical density measured at 785 and 420 mμ. Typical results were:

Sample no.	1	2	3	4	5	6	7	8	9	10
Concn. (10^{-3}M)	0·0	0·814	1·40	2·90	4·20	6·00	7·00	7·90	8·60	8·40
$[M]_D^{22}$	0·0°	+49·3°	+25·5°	+7·69°	0·0°	0·0°	0·0°	0·0°	0·0°	0·0°
Sample no.	11	12	13	14	15	16	17	18	19	
Concn. (10^{-3}M)	7·20	5·70	5·20	4·30	3·40	2·60	1·40	0·50	0·0	
$[M]_D^{22}$	0·0°	0·0°	0·0°	−1·03°	−2·63°	−7·72°	−31·8°	−44·6°	0·0°	

For each sample the ratio of the measured absorbancy at 424 to that at 785 mμ was 1·60 ± 0·03, thus confirming the chemical homogeneity of the complex.

Attempted Preparations of 1,3-*Dimethyl*-1,5-*diphenylformazan*.—(*a*) 3-Methyl-1,5-diphenylformazan (5 g.), sodium ethoxide (from sodium, 0·54 g., and ethanol, 50 ml.), and methyl iodide (2 ml.) in ethanol (55 ml.) were heated under reflux. After removal of sodium iodide and solvent a deep red viscous product was obtained.

(*b*) *Benzaldehyde* N′-*methyl*-N′-*phenylhydrazone* [from benzene–light petroleum (1 : 1)] was pale yellow, with m. p. 104° (Found: C, 80·1; H, 6·6; N, 13·3. $C_{14}H_{14}N_2$ requires C, 80·0; H, 6·7; N, 13·3%). Attempts to couple this hydrazone (dissolved in pyridine) with benzenediazonium chloride gave only starting material.

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