Synthesis of some Phenyl-substituted Stilbenediamines and their Complexes with Nickel(II)

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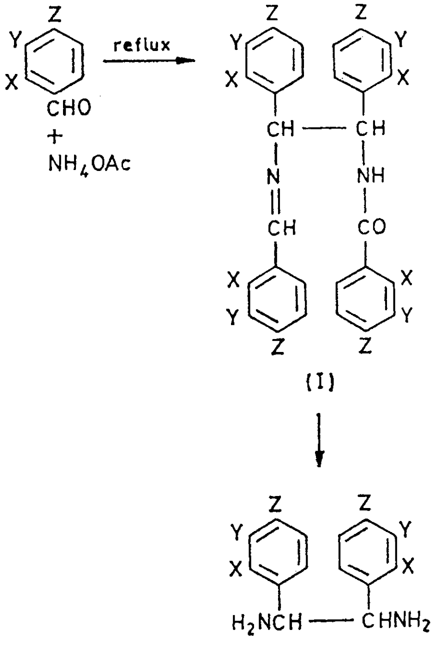
Seven *meso*-diamines, 1,2-bis-2-chloro-, 1,2-bis-3-chloro-, 1,2-bis-4-chloro-, 1,2-bis-4-fluoro-, 1,2-bis-3,4-dichloro-, 1,2-bis-3-nitro-, and 1,2-bis-3-methylphenylethylenediamine have been prepared by reaction of the corresponding benzaldehyde with ammonium acetate and hydrolysis of the resulting *N*-benzoyl-*N'*-benzylidene-*meso*-1,2-diphenylethylenediamine with sulphuric acid. These diamines were each complexed with nickel(II) acetate, nitrate, perchlorate, and chloride to produce a variety of octahedral (blue, paramagnetic) or square planar (yellow diamagnetic) bis(diamine)nickel(II) salts which have been studied by i.r. and electronic spectroscopy and magnetic techniques.

COMPLEXES of nickel(II) with *meso*-stilbenediamine (1,2-diphenylethylenediamine = stien), the Lifshitz complexes,[1-3] are associated with interesting synthetic and theoretical problems. These $Ni(stien)_2X_2$ salts can occur in both yellow and blue modifications, depending on the nature of X and the degree of hydration,[4] and are sometimes interconvertible. In the case of the anhydrous compounds, it has been found that when X is the anion of a strong mineral acid, *e.g.* ClO_4, Cl, NO_3, the complexes are yellow; however, when X is the anion of an organic acid, *e.g.* acetate, chloroacetate, benzoate, both yellow diamagnetic and blue paramagnetic forms are obtained.

Nyburg *et al.*[5-7] have reinvestigated the *meso* stilbenediamine complexes of nickel dichloroacetate. The *X*-ray crystal structure[7] of the blue tetrahydrate shows the Ni^{II} ion to have octahedral stereochemistry with the two water molecules in the apical positions, while in the unit cell of yellow $[Ni(stien)_2](CHCl_2CO_2)_2,2/3H_2O,3/4EtOH$ there are two molecules with octahedral structure (with apical dichloroacetate ions) and one with planar structure.

In this work, we report the synthesis of seven *meso*-stilbenediamine analogues, which differ from the parent by having substituents of varying size and electron donor properties located on the phenyl rings, *viz.* 1,2-bis-2-chloro- (*o*-Cl-stien), 1,2-bis-3-chloro- (*m*-Cl-stien), 1,2-bis-4-chloro- (*p*-Cl-stien), 1,2-bis-4-fluoro- (*p*-F-stien), 1,2-bis-3,4-dichloro- (3,4-Cl_2-stien), 1,2-bis-3-nitro- (*m*-NO_2-stien), and 1,2-bis-3-methylphenylethylenediamine (*m*-CH_3-stien).

These ligands were prepared by the method of Trippett[8] who, developing the early work of Pinner,[9] found that the compound of alleged formula $C_{42}H_{37}O_2N_3$ formed by refluxing ammonium acetate with benzaldehyde is, in fact, *N*-benzoyl-*N'*-benzylidene-*meso*-1,2-diphenylethylenediamine (I; X = Y = Z = H). Hydrolysis of this with sulphuric acid, followed by neutralisation of the reaction mixture with ammonia, yielded *meso*-stilbenediamine[10] (II; X = Y = Z = H).



The method employed here, consisted of refluxing the parent benzaldehyde with twice its weight of ammonium acetate for 3 h. The product formed was initially identified as being of the *N*-benzoyl-*N'*-benzylidene type, or otherwise, from its i.r. spectrum, with characteristic frequencies[11] at $\nu_1 = 3120$—3330 (NH stretch), $\nu_2 =$ 1630—1680 (C=O and C=N stretch), and $\nu_3 = 1510$—1570 cm^{-1} (NH bend). Table 1 lists synthetic, analytical, and i.r. data for these intermediates.

Of the substituted benzaldehydes used in this work, six gave intermediates of a type similar to benzaldehyde,

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[1] I. Lifshitz, J. G. Bos, and K. M. Dijkema, *Z. anorg. Chem.*, 1939, **242**, 97.

[2] I. Lifshitz and J. G. Bos, *Rec. Trav. chim.*, 1940, **59**, 407.

[3] F. Hein and H. Muller, *Z. anorg. Chem.*, 1956, **283**, 172.

[4] A. E. Martell and M. Calvin, 'Chemistry of the Metal Chelate Compounds,' Prentice-Hall, Englewood Cliffs, New Jersey, 1952, pp. 283—284.

[5] S. C. Nyburg, J. S. Wood, and W. C. E. Higginson, *Proc. Chem. Soc.*, 1961, 297.

[6] W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 463.

[7] S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 468.

[8] S. Trippett, *J. Chem. Soc.*, 1957, 4407.

[9] A. Pinner, *Ber.*, 1889, **22**, 1598.

[10] M. N. H. Irving and R. M. Parkins, *J. Inorg. Nuclear Chem.*, 1965, **27**, 270.

[11] J. R. Dyer, 'Applications of Absorption Spectroscopy of Organic Compounds,' Prentice-Hall, New Jersey, 1965, p. 35.

which could be hydrolysed to give *meso*-stilbenediamines; one, α-naphthaldehyde, gave the expected intermediate but failed to hydrolyse and a further nine failed to undergo the desired condensation. Completely unreactive were 2,6- and 2,4-dichlorobenzaldehyde: 2-, 3-, and 4-hydroxybenzaldehyde and pyridine-2-carbaldehyde rapidly produced black tars: 2-amino- and 3-dimethylamino-benzaldehyde slowly formed black mobile liquids with most of the aldehyde being recovered unchanged and the product from *p*-tolualdehyde could not be identified. Analytical data for the product from 2-chlorobenzaldehyde did not correspond to (I; X = Z = H, Y = Cl) but rather to the partially hydrolysed *N*-2-chlorobenzoyl derivative. Since hydrolysis to the required diamine proceeded satisfactorily, this intermediate was not further characterised.

TABLE 1

Analytical and physical data for some *N*-benzoyl-*N'*-benzylidene-*meso*-1,2-diphenylethylenediamines (I) and some *meso*-stilbenediamines (II)

Compound (I)	M.p. (t/°C)	Found (%) C	Found (%) H	Found (%) N	Empirical formula	Required (%) C	Required (%) H	Required (%) N	Yield (%)	1 (cm^{-1})	2 (cm^{-1})	3 (cm^{-1})
X = Y = Z = H	259—260 [a]								65 [b]	3400m	1635s	1520s
X = Cl, Y = Z = H	139—140	61·5	3·8	5·2	$C_{28}H_{20}ON_2Cl_4$	62·0	3·7	5·2	59 [c]	3450m	1640s	1540s
Y = Cl, X = Z = H	156—157	59·9	4·1	6·4	$C_{21}H_{17}ON_2Cl_3$ [d]	60·0	4·0	6·7	82 [c]	3310s	1640s	1535s
Z = Cl, X = Y = H	247—248 [e]								67 [c]	3320m	1635s	1538m
Y = Z = Cl, X = H	220—221	49·5	2·5		$C_{28}H_{16}ON_2Cl_8$	49·4	2·4		72 [f]	3310s	1640s	1525m
Z = F, X = Y = H	219—220	70·6	4·5	6·1	$C_{28}H_{20}ON_2F_4$	70·6	4·2	5·9	48 [c]	3340s	1640s	1530s
Y = CH_3, X = Z = H	155—156	78·3 [g]	7·2	6·3	$C_{32}H_{32}ON_2$	83·5	7·0	6·1	54 [c]	3310s	1643s	1542m
X = Z = H, Y = NO_2										3410m	1645m	1520s
Z = H, X + Y = C_4H_4										3350m	1635m	1555m
Compound (II)												
X = Y = Z = H	120—121 [h]								55 [i]			
X = Cl, Y = Z = H	129—130	59·8	5·1	10·1	$C_{14}H_{14}N_2Cl_2$	59·8	5·0	10·0	48 [i]			
X = Z = H, Y = Cl	147—148	59·8	4·8	9·9	$C_{14}H_{14}N_2Cl_2$	59·8	5·0	10·0	31 [i]			
X = Y = H, Z = Cl	136—137 [j]				$C_{14}H_{14}N_2Cl_2$				56 [i]			
X = H, Y = Z = Cl	139—140	47·9	3·5	7·8	$C_{14}H_{12}N_2Cl_4$	48·0	3·4	8·0	47 [i]			
X = Y = H, Z = F	100—101	68·3	5·8	11·2	$C_{14}H_{14}N_2F_2$	67·8	5·7	11·3	34 [i]			
X = Y = H, Z = CH_3	139—140	79·8	8·3	11·5	$C_{16}H_{20}N_2$	80·0	8·3	11·7	46 [i,k]			
X = Z = H, Y = NO_2	188—189 [l]								40			

[a] Ref. 8 reports m.p. 258—259 °C. [b] From butan-1-ol. [c] From ethanol. [d] Corresponding to *N*-2-chlorobenzoyl-*meso*-1,2-bis-3-chlorophenylethylenediamine. [e] Ref. 8 reports m.p. 249 °C. [f] From 3 : 1 propan-2-ol : methanol. [g] This figure is unexplicably low. [h] Ref. 8 reports m.p. 120·5—121·5 °C. [i] Based on the weight of intermediate used. [j] Ref. 8 reports m.p. 137—138 °C. [k] From methanol. [l] Ref. 8 reports m.p. 189—190 °C.

The seven intermediates were hydrolysed by refluxing each with 70% sulphuric acid (50% for the product from 2-nitrobenzaldehyde) for 1 h, followed by boiling for *ca.* 3 h with the addition of water at regular intervals to prevent concentration of the reaction mixture. The stilbenediamines were precipitated by careful neutralisation of the cooled reaction mixture, with 1 : 1 ammonia (d 0·880)-water.

The amines were extracted with ether, and after removal of the solvent, were recrystallised from light petroleum (b.p. 50—70 °C); the analytical data are listed in Table 1.

The stereochemistry of the ligands was assumed to be *meso*, as the reaction between benzaldehyde and ammonium acetate gives stilbenediamine in this configuration.[8,10] However, the mechanism of this stereospecific reaction remains obscure and both benzoin-type [8] and amarine-type [10] condensation have been proposed.

The seven stilbenediamine ligands (Table 1) have been used to prepare Ni^{II} complexes of the general formula $Ni(diamine)_2X_2,nH_2O$ (X = ClO_4, NO_3, Cl, or AcO and n = 0, 1, or 2). In many cases, interconvertible yellow and blue modifications were observed. The general procedure was to react hot alcoholic (methanol or ethanol) solutions of the Ni^{II} salt with two equivalents of the diamine dissolved in the hot alcohol. In most cases, the bis-diamine complex was precipitated immediately in good yield, but occasionally, solvent evaporation and/or ice cooling was required. Recrystallisation of the product was normally performed by Soxhlet extraction into a suitable solvent mixture (usually methanol : propan-2-ol). Analytical data for the complexes and their physical characteristics are reported in Table 2.

In all cases, the initial product from $Ni(ClO_4)_2,6H_2O$ was the yellow diamagnetic square planar $[Ni(diamine)_2](ClO_4)_2$, but with 3,4-Cl_2-stien and *m*-NO_2-stien the yellow crystals rapidly adsorbed atmospheric water to form the blue paramagnetic octahedral dihydrate. The i.r. spectra of these blue products showed only bands due to ionic ClO_4^- (*e.g.* the band at 615 cm^{-1} was unchanged in going from the anhydrous to the dihydrate) and the change in stereochemistry is probably due to co-ordination of water in the axial positions to form the octahedral *trans*-$[Ni(diamine)_2(OH_2)_2](ClO_4)_2$ salts. The solid-state electronic spectra [*] are also consistent with this interpretation although the possibility of five-co-ordinate species cannot be completely ruled out. A *cis*-diamine configuration is unlikely because of steric inter-

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[*] The data have been deposited in Supplementary Publication No. SUP 20744 (6 pp.) For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

action between the phenyl rings of adjacent diamine ligands.

For the nitrate salts, *o*-, *m*-, and *p*-Cl-stien and *p*-F-stien gave yellow diamagnetic complexes, $[Ni(diamine)_2](NO_3)_2$, but the first formed product with stien was, on some occasions, green. Recrystallisation by extraction into methanol gave the yellow $[Ni(stien)_2](NO_3)_2$, with the blue octahedral $Ni(stien)_2(NO_3)_2$ remaining as a methanol-insoluble powder. With *m*-NO_2- and 3,4-Cl_2-stien, the blue anhydrous dinitrato-salts were obtained directly. These latter give yellow solutions in ethanol and acetone–water but slow evaporation yields only the blue complexes. The splitting of ν_3 (doubly degenerate stretch) and ν_4 (doubly degenerate in-plane bending) in the i.r. spectra of the blue complexes is characteristic of nitrate co-ordinated as a unidentate ligand, while the i.r. spectra * of the yellow salts are characteristic of ionic nitrate. Although the blue salts are formulated here as octahedral dinitrato-complexes, we cannot rule out the possibility of 5-co-ordinate species. The conductivity of the related acetato-complexes (Table 2, footnotes *u* and *v*), however, indicates both acetate groups are co-ordinated, and we believe a similar situation occurs in these nitrato-complexes.

The chloride salts with these stilbenediamine ligands, gave the most variation in colour and degree of hydration. With stien and *m*-Me-stien, yellow dihydrates were obtained which could be thermally dehydrated to give the orange anhydrous form. These anhydrous complexes readily hydrated on exposure to moist air but no other colour changes were observed. Yellow dihydrates were also obtained for *o*-Cl-, *m*-Cl, *p*-Cl-, and 3,4-Cl_2-stien but these undergo a series of dehydration and anation

TABLE 2

Analytical and physical properties of some $Ni(diamine)_2X_2,nH_2O$ salts

Compound (colour)	Found (%) Ni (or N)	C	H	Empirical formula	Required (%) Ni	C	H	$\mu_{eff} \pm 0.4$/ B.M. 291 K	Yield (%)
$Ni(stien)_2(ac)_2$ (blue)	9·7	63·9	6·4	$C_{32}H_{38}O_4N_4Ni$	9·8	63·9	6·3	3·11	63 [a]
$Ni(stien)_2(NO_3)_2$ (yellow)	9·9	55·5	5·6	$C_{28}H_{32}O_6N_6Ni$	9·7	55·4	5·3	dia [b]	32 [c]
(blue)	9·6	55·2	5·3		9·7	55·4	5·3	3·16	28 [d]
$Ni(stien)_2(ClO_4)_2$ (yellow)	8·5	49·4	4·8	$C_{28}H_{32}O_8N_4Cl_2Ni$	8·6	49·3	4·7	dia	68 [e]
$Ni(stien)_2Cl_2,2H_2O$ [f] (yellow)	9·9	58·0	6·2	$C_{28}H_{36}O_2N_4Cl_2Ni$	10·0	57·0	6·1	dia	80 [c]
$Ni(stien)_2Br_2$ (yellow)	8·6	53·0	5·0	$C_{28}H_{32}N_4Br_2Ni$	8·7	52·3	5·0	dia	82 [g]
$Ni(stien)_2I_2$ (orange)	8·2	46·0	4·6	$C_{28}H_{32}N_4I_2Ni$	8·0	45·7	4·4	dia	78 [e]
Ni(*o*-Cl-stien)$_2$(ac)$_2$,CH_3OH [u] (blue)	7·6	51·2	5·0	$C_{33}H_{38}O_5N_4Cl_4Ni$	7·6	51·4	4·9	3·13	57 [e]
Ni(*o*-Cl-stien)$_2$(NO_3)$_2$ (yellow)	8·0	45·3	4·0	$C_{28}H_{28}O_6N_6Cl_4Ni$	7·9	45·1	3·8	dia	90 [h]
Ni(*o*-Cl-stien)$_2$(ClO_4)$_2$ (yellow)	7·1	41·2	3·6	$C_{28}H_{28}O_8N_4Cl_6Ni$	7·2	41·1	3·5	dia	97 [h]
Ni(*o*-Cl-stien)$_2$$Cl_2$,$2H_2O$ (yellow)	8·1	45·9	4·6	$C_{28}H_{32}O_2N_4Cl_6Ni$	8·1	46·2	4·4	dia	91 [e]
Ni(*o*-Cl-stien)$_2$$Cl_2$ (pink)	7·9	48·6	4·0	$C_{28}H_{28}N_4Cl_6Ni$	8·0	48·6	4·1	dia	*h*
Ni(*m*-Cl-stien)$_2$(ac)$_2$,H_2O (blue)	7·9	50·7	4·9	$C_{32}H_{36}O_5N_4Cl_4Ni$	7·4	50·7	4·8	3·12	73 [c]
Ni(*m*-Cl-stien)$_2$(NO_3)$_2$ (yellow)	11·3	45·0	4·0	$C_{28}H_{28}O_6N_6Cl_4Ni$	11·3	45·1	3·8	dia	98 [i]
Ni(*m*-Cl-stien)$_2$(ClO_4)$_2$ (yellow)	6·5	41·6	3·7	$C_{28}H_{28}O_8N_4Cl_6Ni$	6·8	41·1	3·5	dia	73 [c]
Ni(*m*-Cl-stien)$_2$$Cl_2$,$2H_2O$ (blue)	7·4	46·3	4·5	$C_{28}H_{32}O_2N_4Cl_6Ni$	7·7	46·2	4·4	3·71	*j*
Ni(*p*-Cl-stien)$_2$(ac)$_2$ (blue)	7·9	52·0	4·7	$C_{32}H_{34}O_4N_4Cl_4Ni$	8·0	52·0	4·6	3·09	51 [k]
Ni(*p*-Cl-stien)$_2$(NO_3)$_2$ (yellow)	8·2	45·3	4·2	$C_{28}H_{28}O_6N_6Cl_4Ni$	7·9	45·1	3·8	dia	73 [l]
Ni(*p*-Cl-stien)$_2$(ClO_4)$_2$ (yellow)	7·0	41·3	3·7	$C_{28}H_{28}O_8N_4Cl_6Ni$	7·2	41·1	3·5	dia	57 [e]
Ni(*p*-Cl-stien)$_2$$Cl_2$,$2H_2O$ (yellow)	8·2	46·8	4·5	$C_{28}H_{32}O_2N_4Cl_6Ni$	8·1	46·2	4·4	dia	87 [m]
Ni(*p*-Cl-stien)$_2$$Cl_2$,$H_2O$ (red)	8·4	47·5	4·5	$C_{28}H_{30}ON_4Cl_6Ni$	8·3	47·3	4·3	var. [t]	*h*
Ni(3,4-Cl_2-stien)$_2$(ac)$_2$ (blue)	6·6	43·7	4·0	$C_{32}H_{30}O_4N_4Cl_8Ni$	6·7	43·8	3·4	3·01	85 [e]
Ni(3,4-Cl_2-stien)$_2$(NO_3)$_2$ (blue)	6·6	39·1	3·5	$C_{28}H_{24}O_6N_6Cl_8Ni$	6·7	38·1	3·7	3·00	67 [h]
Ni(3,4-Cl_2-stien)$_2$(ClO_4)$_2$ (yellow)	6·4	35·2	2·8	$C_{28}H_{24}O_8N_4Cl_{10}Ni$	6·2	35·1	2·5	dia	88 [e]
Ni(3,4-Cl_2-stien)$_2$(ClO_4)$_2$,$2H_2O$ [n] (blue)	6·1	34·1	3·0	$C_{28}H_{28}O_{10}N_4Cl_{10}Ni$	5·9	33·8	2·8	3·18	
Ni(3,4-Cl_2-stien)$_2$$Cl_2$,$2H_2O$ (yellow)	6·8	38·8	3·2	$C_{28}H_{28}O_2N_4Cl_{10}Ni$	6·8	38·9	3·2	dia	84 [o]
Ni(3,4-Cl_2-stien)$_2$$Cl_2$ (green)	6·9	40·7	3·0	$C_{28}H_{24}N_4Cl_{10}Ni$	7·1	40·5	2·9	3·16	*p*
Ni(3,4-Cl_2-stien)$_2$$Br_2$,$2H_2O$ [q] (yellow)	6·3	35·4	2·8	$C_{28}H_{28}O_2N_4Br_2Cl_8Ni$	6·2	35·2	2·9	dia	78 [e]
Ni(*m*-NO_2-stien)$_2$(ac)$_2$ (blue)	(14·1)	49·0	4·2	$C_{32}H_{34}O_{16}N_8Ni$	(14·3)	49·2	4·4	3·43	32 [o]
Ni(*m*-NO_2-stien)$_2$(NO_3)$_2$ (blue)	(17·3)	43·1	3·8	$C_{28}H_{28}O_{14}N_{10}Ni$	(17·8)	42·7	3·6	3·16	61 [o]
Ni(*m*-NO_2-stien)$_2$)ClO_4)$_2$ (yellow)	(12·9)	38·8	3·9	$C_{28}H_{28}O_{16}N_8Cl_2Ni$	(13·0)	40·0	3·3	dia	80 [o]
Ni(*m*-NO_2-stien)$_2$(ClO_4)$_2$,$2H_2O$ [r] (blue)	(12·1)	37·7	3·8	$C_{28}H_{32}O_{18}N_8Cl_2Ni$	(12·5)	37·4	3·6	3·13	
Ni(*m*-NO_2-stien)$_2$$Cl_2$ (green)	(15·1)	45·9	4·0	$C_{28}H_{28}O_8N_8Cl_2Ni$	(15·3)	45·8	3·8	3·16	73 [o]
Ni(*m*-CH_3-stien)$_2$(ac)$_2$,$2CH_3OH$ [v] (blue)	(8·2)	63·3	7·3	$C_{38}H_{54}O_6N_4Ni$	(7·8)	63·2	7·5	3·29	47 [o]
Ni(*m*-CH_3-stien)$_2$$Cl_2$,$2H_2O$ [s] (yellow)	(8·3)	59·1	6·6	$C_{32}H_{44}O_2N_4Cl_2Ni$	(8·7)	59·4	6·8	dia	97 [e]
Ni(*m*-CH_3-stien)$_2$$Cl_2$ (orange)	(9·1)	63·3	7·0	$C_{32}H_{40}N_4Cl_2Ni$	(9·2)	63·0	6·6	dia	*o*
Ni(*m*-CH_3-stien)$_2$(ClO_4)$_2$ (yellow)	(7·6)	52·0	5·6	$C_{32}H_{40}O_8N_4Cl_2Ni$	(7·6)	52·0	5·4	dia	64 [o]
Ni(*p*-F-stien)$_2$(ac)$_2$,$2H_2O$ (yellow)	(7·9)	54·0	5·9	$C_{32}H_{38}O_6N_4F_4Ni$	(7·9)	54·2	5·4	dia	46 [o]
Ni(*p*-F-stien)$_2$(ac)$_2$ (blue)	(8·2)	56·4	5·3	$C_{32}H_{24}O_4N_4F_4Ni$	(8·3)	57·1	5·1	3·95	*i*
Ni(*p*-F-stien)$_2$(NO_3)$_2$ (yellow)	(12·5)	49·4	4·4	$C_{28}H_{28}O_6N_6F_4Ni$	(12·4)	49·5	4·1	dia	78 [i]

[a] From 1 : 3 ethanol : propan-2-ol. [b] dia = diamagnetic. [c] From methanol. [d] Insoluble in methanol. [e] From 1 : 3 methanol : propan-2-ol. [f] Weight loss on heating found, 6·7%; required for loss of $2H_2O$, 6·1%. [g] From 2 : 3 methanol : propan-2-ol. [h] From 3 : 1 methanol : propan-2-ol. [i] From ethanol. [j] From 5 : 10 : 1 methanol : propan-2-ol : water. [k] From 3 : 1 ethanol : propan-2-ol. [l] From 1 : 2 ethanol : propan-2-ol. [m] From 3 : 1 methanol : water. [n] Weight loss on heating, found 3·7%; required for $2H_2O$, 3·6%. [o] Not recrystallised. [p] From 4 : 1 methanol : propan-2-ol. [q] Weight loss on heating, found 3·6%; required for $2H_2O$, 3·8%. [r] Weight loss on heating, found 4·2%; required for $2H_2O$, 4·0%. [s] Weight loss on heating, found 6·0%; required for $2H_2O$, 5·6%. [t] Four measurements over 24 h gave consistent values of 1·20, 1·71, 0, and 0 B.M. [u] A 10^{-3}M-solution in methanol has $\Lambda_M = 46.7$ at 25 °C. [v] A 10^{-3}M-solution in methanol has $\Lambda_M = 62.7$ at 25 °C.

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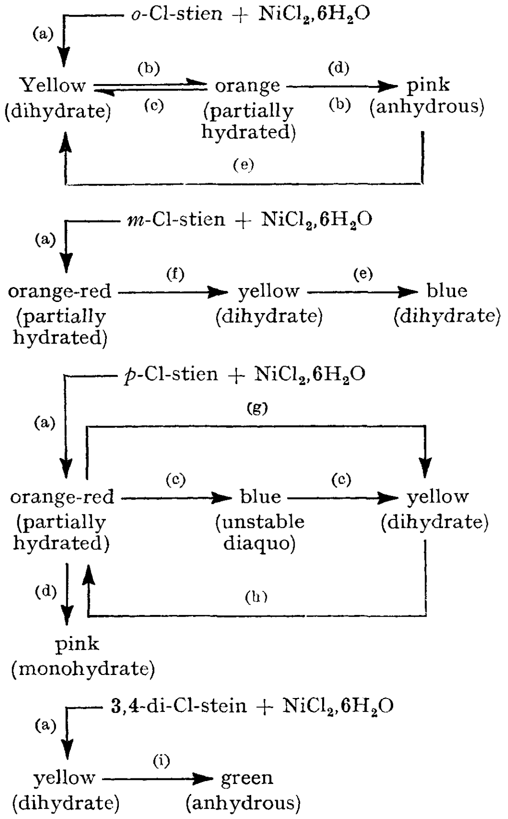
* Same note as on page 1938.

reactions to give orange, pink, green, or blue products; the reaction sequences are presented in the Scheme.



SCHEME Transformations observed in the Ni(diamine)$_2$Cl$_2$,nH$_2$O systems. Reagents or conditions are (a) in methanol; (b) heat at 110 °C; (c) stand in air; (d) recrystallise from 3 : 1 methanol : propan-2-ol; (e) recrystallise from 3 : 1 methanol : propan-2-ol containing a small amount of water; (f) stand in solution; (g) recrystallise from 10 : 1 methanol : water; (h) wash with methanol; (i) recrystallise from 4 : 1 methanol : propan-2-ol

With *m*-NO$_2$-stien, the green anhydrous dichloride was the only product. The colour changes can probably be rationalised in accordance with the following structures: [Ni(diamine)$_2$]Cl$_2$,2H$_2$O (yellow, diamagnetic, square planar); [Ni(diamine)$_2$]Cl$_2$ (orange or pink, diamagnetic, square planar); [Ni(diamine)$_2$(OH$_2$)$_2$]Cl$_2$ (blue, paramagnetic, octahedral); Ni(diamine)$_2$Cl$_2$ (green, paramagnetic, octahedral). The magnetic susceptibility data support these assignments, although the figure (Table 2) for blue [Ni(*m*-Cl-stien)$_2$(OH$_2$)$_2$]Cl$_2$ is abnormally high. Attempts to prepare a green Ni(3,4-di-Cl-stien)$_2$-Br$_2$ were not successful, and only the yellow [Ni(3,4-di-Cl-stien)$_2$]Br$_2$,2H$_2$O was obtained. Presumably steric factors prevent the larger bromide ions from occupying the apical positions.

The acetate salts represent the most complete series for which blue octahedral products were obtained, and their solubility in methanol allowed a more complete investigation of their electronic spectra.* Only with *p*-F-stien was a yellow dihydrate obtained [blue Ni(stien)$_2$(ac)$_2$ also gave a yellow solution in water] and, in general, the anhydrous blue acetato-complexes were formed. However, the acetate salts of *o*-Cl-stien, *m*-Me-stien, and *m*-Cl-stien crystallised with 1 and 2 mol. equiv. of methanol and 1 mol. equiv. of water, respectively. The electronic spectra and low conductivity in methanol (Table 2) indicate that these blue complexes have an octahedral stereochemistry with both acetate ligands co-ordinated, *i.e.* Ni(diamine)$_2$(ac)$_2$. The ligand-field parameters * calculated on the basis of the observed absorption spectra are very similar and it is apparent that, for the acetates at least, the ligand-field strengths of these diamines are similar, and that changes in stereochemistry arising from changes in the ligand are predominantly due to steric factors. An attractive assumption would be that an increase in the size and number of substituents on the phenyl rings (*i.e.* increasing the steric hindrance in the axial positions) should reflect in an increasing tendency to square-planar formation. In fact, the reverse seems to occur. Thus, with the perchlorate salts, both *m*-NO$_2$- and 3,4-Cl$_2$-stien (the ligands with the largest substituents) gave blue octahedral bis-diamine diaquo-complexes, while for the other ligands with less-bulky substituents only yellow planar complexes were observed. The nitrate and chloride salts show similar effects, but the trend with the acetates is not clear. We note, however, that *m*-NO$_2$-stien gives only a blue acetato-complex, whereas with *p*-F-stien, the yellow form is the most stable.

Models indicate that even with bulky substituents on the phenyl rings, there are configurations with relatively open positions in the axial directions above and below the NiN$_4$ plane, but such substituents do not allow free rotation of the benzene rings. It is possible that for those ligands where the axial phenyl groups perpendicular to the chelate ring are free to rotate, that the axial Ni^{II} positions would be more hindered than those where rotation is restricted. In any event, it is evident that factors other than phenyl substituents are important in establishing the subtle differences between octahedral and square-planar configurations, as with all the ligands used, at least one salt of each type was obtained.

EXPERIMENTAL

The commercially available aldehydes and Ni(ac)$_2$,4H$_2$O, NiCl$_2$,6H$_2$O, and Ni(NO$_3$)$_2$,6H$_2$O were used without further purification. Ni(ClO$_4$)$_2$,6H$_2$O was made from NiCO$_3$ and HClO$_4$. Analytical data are presented in Tables 1 and 2.

meso-*Stilbenediamines*.—The *N*-benzoyl-*N'*-benzylidene-*meso*-1,2-diphenylethylenediamine intermediates were prepared using the method of Trippet,[8] usually with 10—20 g of substituted benzaldehyde and 20—40 g of ammonium acetate (Table 1). These intermediates (5—10 g) were hydrolysed with 70% H$_2$SO$_4$ (50—100 ml) to yield 1—3 g of recrystallised diamine (Table 1).

Bis(diamine)nickel(II) *Perchlorate Salts*.—A hot methanolic solution (20—50 ml) of the diamine (2 equiv. on a 0·5—2 g scale) was added with stirring to a hot methanolic solution (20—50 ml) of Ni(ClO$_4$)$_2$,6H$_2$O (1 equiv.). The yellow crystalline precipitate that deposited (usually within 1 h)

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* Same note as on page 1938.

was collected and recrystallised by Soxhlet extraction into a suitable solvent (see Table 2). Variation of the initial conditions involved the use of butanol as a solvent for *m*-NO_2-stien and ethanol for 3,4-Cl_2- and *m*-Me-stien. The anhydrous yellow products from 3,4-Cl_2- and *m*-NO_2-stien readily adsorbed atmospheric water (30 min at room temperature) forming the blue diaquo-salts.

Bis(diamine)nickel(II) *Nitrate Salts*.—These salts were prepared as for the perchlorates but with ethanol as a solvent for stien and *p*-Cl-stien and butanol for *m*-NO_2-stien. With stien, the initial yellow precipitate occasionally changed to green. Recrystallisation of this material by Soxhlet extraction with methanol yielded yellow $[Ni\text{-}stien)_2](NO_3)_2$ from the solvent and blue $Ni(stien)_2(NO_3)_2$ remained in the extraction thimble. With 3,4-Cl_2- and *m*-NO_2-stien, the initial products were blue and anhydrous, while for the remaining ligands, the yellow anhydrous salts were deposited. All products were unchanged upon recrystallisation.

Bis(diamine)nickel(II) *Chloride Salts*.—These salts were prepared as for the perchlorates but with ethanol as a solvent for stien and *m*-NO_2-stien. The initial product was the yellow dihydrate when stien, *o*-Cl-stien, 3,4-Cl_2-stien, *m*-Me-stien, and *m*-Cl-stien were used. Recrystallisation of the crude yellow $[Ni(m\text{-}Cl\text{-}stien)_2]Cl_2,nH_2O$ (n = 2?) from 3 : 1 methanol: propan-2-ol gave an orange product containing some water (i.r.). This was converted to the blue diaquo-compound by Soxhlet extraction into 5 : 10 : 1 methanol : propan-2-ol : water; this blue product was stable *in vacuo*, in air and to heat (110 °C for 15 min). Thermal dehydration of the yellow dihydrates (110 °C for 30 min) from stien, *o*-Cl-stien, and *m*-Me-stien gave the orange, pink, and orange anhydrous salts, respectively, which slowly reform the dihydrates on exposure to air. Pink $[Ni(o\text{-}Cl\text{-}stien)_2]Cl_2$ was also formed on extraction of the yellow dihydrate into 3 : 1 methanol : propan-2-ol.

Reaction of $NiCl_2,6H_2O$ and *p*-Cl-stien in methanol initially formed an orange product, which on drying in air changed through blue to the yellow dihydrate. This dihydrate was also obtained from the crude product by extraction into 3 : 1 methanol : water. Washing of the yellow dihydrate with methanol produced a colour change to orange which then behaved as the original orange precipitate when dried in air. The intermediate blue diaquo(?) compound was unstable in air, rapidly reverting to the yellow dihydrate. Recrystallisation of the orange (partially hydrated?) product by extraction into 3 : 1 methanol : propan-2-ol formed the red monohydrate.

Recrystallisation of the yellow $[Ni(3,4\text{-}Cl_2\text{-}stien)_2]Cl_2,2H_2O$ by extraction into 4 : 1 methanol : propan-2-ol produced the green anhydrous dichloro-compound, which did not appear to revert to the yellow dihydrate. A similar green material was the initial reaction product with $NiCl_2,6H_2O$ and *m*-NO_2-stien.

Bis(diamine)nickel(II) *Acetate Salts*.—These blue anhydrous complexes were prepared as for the perchlorate salts. As the solubility in methanol is quite high, solvent reduction and ice cooling facilitated the isolation. With *m*-Cl-stien and *m*-Me-stien, solvent reduction produced a green gum, which on trituration with ether, formed a violet powder. Recrystallisation by extraction into methanol produced the pure complex. With *p*-Cl-stien, the initially precipitated violet powder slowly produced blue crystals (probably hydrated) when left in contact with the solution. These were reconverted to a violet powder by dehydration at 110 °C for 5 min. Recrystallisation by extraction into 3 : 1 methanol : propan-2-ol produced the pure product and a green mother liquor which deposited green crystals after *ca.* 24 h. These were not characterised.

The reaction of $Ni(ac)_2,4H_2O$ with 3,4-Cl_2-stien proceeded normally and recrystallisation of the crude product produced blue $Ni(3,4\text{-}Cl_2\text{-}stien)_2(ac)_2$. Slow evaporation of the mother liquor from the recrystallisation yielded both yellow and blue crystals, while evaporation of a 1 : 1 acetone : water solution of the anhydrous complex gave a muddy yellow precipitate. Attempted recrystallisation from 1 : 1 acetone : water was not successful (hydrolytic decomposition occurred) and this yellow material was not characterised further.

With *p*-F-stien, the initial product was the yellow $[Ni(p\text{-}F\text{-}stien)_2](ac)_2,2H_2O$ which was converted into the blue anhydrous form by heating at 110 °C for 20 min.

Instrumentation.—Infrared spectra were made using Nujol mulls between KBr plates and were recorded in the 4000—400 cm^{-1} range on either a Shimadzu IR 27G or Perkin-Elmer 337 spectrophotometer. Solution absorption spectra were recorded on a Shimadzu MPS 50L spectrophotometer and reflectance spectra were recorded using a Beckman DK-2A instrument with MgO as a standard. Magnetic susceptibilities were determined by the Gouy method using $[Ni(en)_3]S_2O_3$ as a calibrant.[12] All measurements were duplicated and the molar susceptibility was corrected for diamagnetism using Pascal constants.[13] Conductivity measurements were determined at 25 °C using a Phillips PR9550/01 bridge and a cell with removable dip-type electrodes. The cell was calibrated with standard KCl solution.

Analyses.—C, H, and N were determined in Professor A. D. Campbell's laboratory at the University of Otago, Dunedin, New Zealand. Ni was determined gravimetrically by precipitation with dimethylglyoxime, the complexes being decomposed by fusion with solid sodium hydrogen sulphate. In the case of the perchlorate complexes decomposition in solution was effected by boiling (4—5 h) with acid solutions of ammonium peroxodisulphate.

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