Chemistry of Polydentate Ligands. Part 2.[1] The Mode of Co-ordination of 6,6′-Dihydrazino-2,2′-bipyridyl Ligands with Nickel(II) and Zinc(II) in Octahedral Complexes

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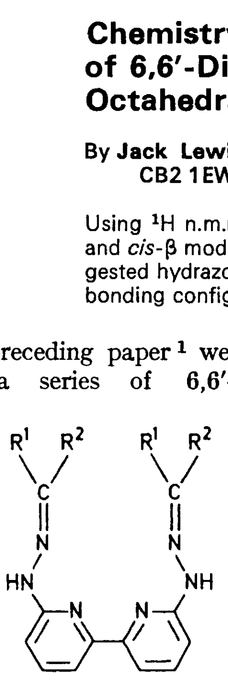
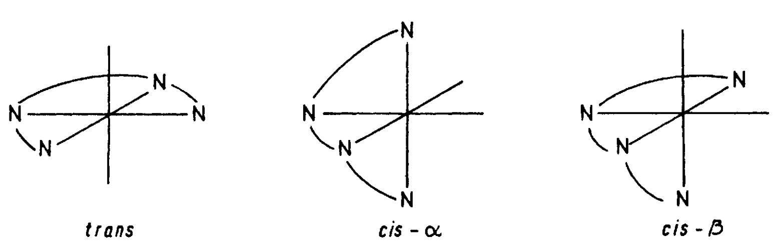
Using ^{1}H n.m.r. and i.r. spectral techniques, the title ligands have been found to co-ordinate to Ni^{II} in both the *cis*-α and *cis*-β modes. With zinc(II), only the *cis*-α geometry is adopted except in the case of the least sterically congested hydrazone, that derived from acetaldehyde, where the *cis*-β complex is also formed. The third alternative bonding configuration, the *trans* structure, has not been observed.



	R¹	R²
(1)	Me	H
(2)	Et	H
(3)	Pr^n	H
(4)	Me	Me
(5)	Et	Me
(6)	Et	Et
(7)	Pr^n	Me

IN the preceding paper[1] we described the manner in which a series of 6,6′-dihydrazino-2,2′-bipyridyl compounds, (1)—(7), can be derived from 6,6′-dihydrazino-2,2′-bipyridylnickel(II) perchlorate by the reaction of the complex with aliphatic aldehydes and ketones. These dihydrazones act as quadridentate ligands, bonding by way of the α-di-imine system and the imino-nitrogen atoms. Since they are linear ligands they can, in principle, co-ordinate in such a way as to give products having the *trans,cis*-α and/or *cis*-β stereochemistry (Scheme).



SCHEME

This report describes work on the bonding configurations adopted by the metal complexes of the ligands.

RESULTS AND DISCUSSION

Molecular models of the *trans* complex show extreme steric hindrance at the point where the two arms of the ligand come together, as, ideally, the two imino-substituents on the different nitrogen centres (R^1, R^2) would occupy the same position in space; it seems unlikely that such a configuration would be adopted and indeed we have no evidence that it ever is. When attempts were made to co-ordinate the dihydrazone derived from acetone, (4), to Pd^{II}, where it might be expected that square-planar geometry (the *trans* structure) is the only accessible stereochemistry, hydrolysis of one imine moiety always preceded co-ordination

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[1] J. Lewis and K. P. Wainwright, preceding paper.

of the resulting unsymmetrical ligand.[2] Such hydrolysis is uncharacteristic of the free ligand even in 4 mol dm^{-3} HCl, but is effective in this case in removing what is probably a prohibitively great steric interaction. An alternative means by which the ligands might co-ordinate in the *trans* configuration would involve rotation about the single bonds to the secondary amines in such a way as to lead to a geometry amenable to the formation of bridged complexes. Molecular-weight studies of some of the complexes suggest that this mode of co-ordination is not adopted.

Of the other two forms the *cis*-β is the more sterically hindered with the imino-carbon substituents *trans* to the secondary amino-group being responsible for the unfavourable interaction. This steric interaction could be minimised in the complexes formed from ligands derived from unsymmetrical aldehydes or ketones by disposing the sterically more bulky group *cis* to the secondary amine rather than *trans*, the position which it predominantly occupies in the free ligand. The *cis*-α form is the least sterically congested of the three configurations, although there is considerable bond strain associated with holding the ligand in the *cis* compared to the *trans* configuration.

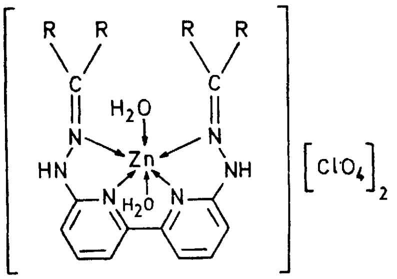
Since rotation about the imino-linkage occurs quite readily,[3] a tendency which may be accounted for by the electronegativity of the nitrogen causing a lowering of the double-bond character by polarisation, it is possible for the alkyl groups on the imino-carbon to arrange themselves in such a manner as to minimise steric repulsions between opposing R groups. Thus, were an unsymmetrical dihydrazone to co-ordinate in the *cis*-β configuration, one would expect to observe a rearrangement that would move the more bulky substituent away from its free-ligand *trans* position to a position *cis* to the secondary amine. Alternatively, should the unsymmetrical ligand co-ordinate so as to give the *cis*-α complex, inspection of molecular models suggests that there should be no significant difference between the concentration of a given substituent in a given position in the complex and that in the free ligand.

Accordingly, by comparing the manner in which the more bulky substituent positions itself, using the ^1H n.m.r. technique already described,[1] it should be possible to determine whether the *cis*-α or *cis*-β geometry is being adopted. The zinc(II) complexes of the series of ligands were prepared for this purpose as their perchlorate salts. By this means it was also possible to determine whether co-ordination occurs *via* the hydrazone form of the ligand or by way of the azo-hydroperoxide with which it exists under aerobic conditions.[1]

The complexes were prepared by the addition of a solution of hexa-aquazinc(II) perchlorate to a methanolic solution of the ligand. The alternative azo-hydroperoxide form of the ligand[1] was shown not to co-ordinate since, when a solution of the ligand was exposed to the atmosphere in refluxing methanol for 10 min before adding the stoicheiometric amount of the metal salt, virtually quantitative yields of the complexes were obtained and analytical data (Table 1) indicated that they were all $[ZnL(OH_2)_2][ClO_4]_2$ adducts and suggested (the ^1H n.m.r. data below confirm this) that the ligand is bound only in its dihydrazone form. Conductivity measurements in methanol established the complexes as 2 : 1 electrolytes.

TABLE 1

Analytical data for complexes of the type



Complex	Derived from	Analysis (%)						Λ *
		Found			Calc.			
		C	H	N	C	H	N	$S\ cm^2\ mol^{-1}$
(8)	(1)	29.8	3.45	14.6	29.6	3.55	14.8	183
(9)	(2)	32.2	3.95	13.9	32.2	4.05	14.1	182
(10)	(3)	34.6	4.35	13.6	34.6	4.50	13.5	177
(11)	(4)	32.4	4.05	14.2	32.2	4.05	14.1	178
(12)	(5)	34.4	4.40	13.3	34.6	4.50	13.5	177
(13)	(6)	36.9	5.00	12.6	36.8	4.95	12.9	184
(14)	(7)	37.0	4.95	12.6	36.8	4.95	12.9	183

* For 10^{-3} mol dm^{-3} solutions in methanol at 22 °C.

The ^1H n.m.r. spectra of the zinc dihydrazone complexes, (8)—(14), were recorded in deuteriomethanol and the data are in Table 2. The data show that the hydrazone form of the ligand alone is co-ordinated, since signals previously assigned to the azo-hydroperoxide[1] were totally absent. This suggests that the oxygen-addition reaction,[1] to form the azo-hydroperoxide, is readily reversible. The fact that oxygen does not attack the co-ordinated ligand is perhaps an indication that oxygen is behaving as an electrophilic species in the initial addition reaction, since co-ordination of the ligand results in enhanced electrophilicity of the imino-carbon and would thus suppress electrophilic attack at that point. Formation of a co-ordinated azo-hydroperoxide would also necessarily lengthen an already long terminal nitrogen–metal bond by increasing the relevant bond angle at the secondary amino-position.

Provided that there is no change in the orders of the chemical shifts associated with protons on *cis*- or *trans*-alkyl groups in the co-ordinated ligand from that previously determined for the free ligand[1] (and the data obtained are compatible with this), there is no marked change in the configuration of any of the ligands on co-ordination, with the exception of that derived from acetaldehyde. The disposition of the various alkyl groups which has been determined from the spectra is

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[2] J. Lewis and K. P. Wainwright, unpublished work.

[3] S. Patai in 'Chemistry of the Amino Group,' Interscience, London, 1968.

given in Table 3. Comparison with the corresponding dispositions in the free ligand (given in parentheses) shows that only in the case of the complex derived from butyraldehyde, (10), is there a slight shift which is outside the bounds of experimental error. The implication of these spectral data is that for complexes (9) — (14) the *cis*-α isomer exists predominantly in solution.

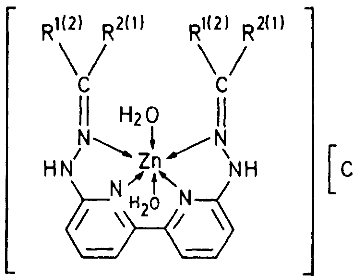
TABLE 2

Proton magnetic resonance data (in τ, *J* values in Hz) for $[ZnL(OH_2)_2][ClO_4]_2$ complexes

Complex	Hydrazone derived from	Aromatic + imino methine	Methylene	Methyl
(8)	Acetaldehyde	1.8—3.1 (m) (8 H)		7.74 (8-line m) (6 H)
(9)	Propionaldehyde	1.8—3.1 (m) (8 H)	7.41 (m) (4 H)	8.68 (t) (*J* 7.5)} (6 H) *cis*-Me 8.73 (t) (*J* 7.5)} *trans*-Me
(10)	Butyraldehyde	1.8—3.1 (m) (8 H)	7.47 (m) (4 H) 8.26 (m) (4 H)	8.91 (t) (*J* 7.5)} (6 H) *cis*-Me 8.94 (t) (*J* 7.5)} *trans*-Me
(11)	Acetone	1.8—2.3 (m) (4 H) 2.8 (d) (*J* 8.0) (2 H)		7.65 (s)} (12 H) *trans*-Me 7.78 (s)} *cis*-Me
(12)	Ethyl methyl ketone	1.8—2.3 (m) (4 H) 2.81 (d of d) (2 H) (J_1 8.0, J_2 1.0)	7.39 (q) (*J* 8.0) (4 H)	7.68 (s)} (6 H) *trans*-Me 7.80 (s)} *cis*-Me 8.78 (t) (*J* 8.0) (6 H)
(13)	Diethyl ketone	1.8—2.3 (m) (4 H) 2.72 (d of d) (2 H) (J_1 8.0, J_2 1.0)	7.30 (q) (*J* 8.0)} (8 H) 7.34 (q) (*J* 8.0)}	8.72 (t) (*J* 8.0)} (12 H) *cis*-Me 8.73 (t) (*J* 8.0)} *trans*-Me
(14)	Methyl n-propyl ketone	1.8—2.3 (m) (4 H) 2.76 (d of d) (2 H) (J_1 8.0, J_2 1.0)	7.35 (t) (*J* 8.0)} (4 H) 7.39 (t) (*J* 8.0)} 8.22 (sxt) (*J* 8.0) (4 H)	7.61 (s)} (6 H) *trans*-Me 7.77 (s)} *cis*-Me 8.89 (t) (*J* 8.0)} (6 H) *cis*-Me 8.92 (t) (*J* 8.0)} *trans*-Me

TABLE 3

Isomeric-distribution data for complexes of the type



Complex	$R^{1(2)}$	$R^{2(1)}$	Percentage of larger group *trans* to the secondary amine [a]
(8)	Me	H	*b*
(9)	Et	H	60 (63)
(10)	Pr	H	45 (60)
(11)	Me	Me	
(12)	Et	Me	76 (85)
(13)	Et	Et	
(14)	Pr	Me	85 (83)

[a] The percentages for the free ligand are given in parentheses; all values ±5%. [b] Both the *cis*-α and *cis*-β isomers are present; no determination was possible.

The spectrum of the zinc complex derived from acetaldehyde, (8), is interesting, showing eight signals in the methyl region instead of the four expected for a single azo-hydroperoxide free compound; it appears that where both substituents on the imino-group are relatively small, namely a proton and a methyl group, both the *cis*-α and *cis*-β forms of the complex are capable of existence. This contrasts quite reasonably with the other members of the series (9)—(14) which all have more bulky imino-substituents and which accordingly form only the *cis*-α isomer.

In order to compare this solution data with the situation in the solid state an analogous series of $[ZnL(NCS)_2]$ complexes, (15)—(21), was prepared; analytical data are given in Table 4. The fact that there are no co-ordinated solvent molecules with the thiocyanate, in contrast to the situation with the perchlorate, salts suggests that both thiocyanates are co-ordinated. The insolubility of the complexes precluded conductivity determinations, but the frequency of the ν(C–S) absorption is in the range 780—860 cm^{-1} normally taken to be indicative of *N*-bonded thiocyanate groups.[4]

Using this counter-ion, one may probe the geometry of the complex [as the disposition of the two NCS groups *trans* to one another leads to only a single C≡N absorption whereas a *cis* disposition leads to splitting of the ν(C≡N) absorption [5]]. Configurational assignments based on this technique, however, have to be treated with some caution, since the coupling between the ν(C≡N) vibrations may be quite small and thus unobservable.[6] Accordingly, the presence of two bands may be evidence for the *cis* isomer, but only one band is not necessarily evidence for the *trans* isomer. Also, since the spectra are being recorded in the solid state, the possibility of solid-state splitting renders the observation of two bands of dubious value. Fortuitously, it seems that such complications due to solid-state splitting are uncommon in complexes of large ligands such as bipyridyl.[7–9]

With the exception of the acetaldehyde derivative, all the $[ZnL(NCS)_2]$ complexes showed either a broad or a split band in the range 2 080—2 125 cm^{-1} (Table 4) indicative of the expected *cis* geometry. In agreement

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[4] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1961, 4590.

[5] R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, 1966, **22**, 1081.

[6] E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.

[7] D. A. Buckingham, F. P. Dwyer, H. A. Goodwin, and A. M. Sargeson, *Austral. J. Chem.*, 1964, **17**, 325.

[8] C. M. Harris and E. D. McKenzie, *J. Inorg. Nuclear Chem.*, 1961, **19**, 372.

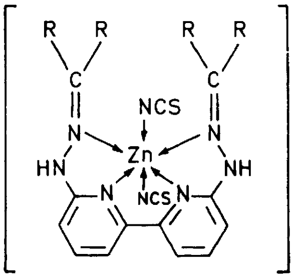
[9] A. A. Schilt, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2677.

with the ^{1}H n.m.r. spectrum, the complex derived from acetaldehyde showed a group of two split bands, one in the above range and one 30 cm^{-1} to lower wavenumbers. Taken in conjunction with the ^{1}H n.m.r. configurational determinations, these observations suggest that the absorptions in the range 2 080—2 125 cm^{-1}, shown by all members of the series, originate from the complex of *cis*-α stereochemistry whilst the lower-frequency absorptions shown only by the acetaldehyde derivative, (15), originate from the complex in the *cis*-β configuration.

The bonding situation with Ni^{II}, however, is different. A corresponding series of complexes, [NiL(NCS)$_2$], (22)—(28), was prepared by reaction of di-isothiocyanatotetrakis(pyridine)nickel(II) with the free ligand. Analytical and conductance data in aqueous solution are

TABLE 4

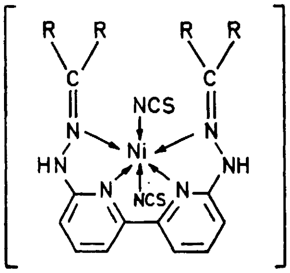
Analytical and spectral data for complexes of the type



		Analysis (%)						I.r. data (±2 cm^{-1})	
		Found			Calc.				
Complex	Derived from	C	H	N	C	H	N	ν(C≡N)	ν(C–S)
(15)	(1)	42.8	3.65	25.2	42.7	3.60	24.9	2 095, 2 083 2 068, 2 056	812
(16)	(2)	45.5	4.35	23.7	45.2	4.20	23.5	2 110br	809
(17)	(3)	47.6	4.85	22.2	47.5	4.80	22.2	2 122, 2 106	829
(18)	(4)	45.3	4.35	23.6	45.2	4.20	23.5	2 121, 2 101	826
(19)	(5)	47.4	4.85	22.1	47.5	4.80	22.2	2 125, 2 108	828
(20)	(6)	49.7	5.30	21.2	49.5	5.30	21.0	2 122, 2 102	828
(21)	(7)	49.2	5.30	20.9	49.5	5.30	21.0	2 099, 2 086	813

TABLE 5

Analytical and spectral data for complexes of the type



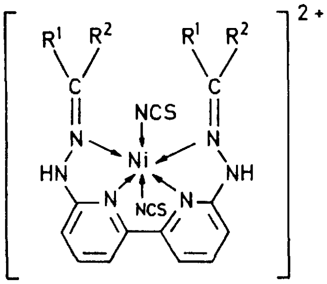
		Analysis (%)						I.r. data (±2 cm^{-1})		Λ [a]
		Found			Calc.					
Complex	Derived from	C	H	N	C	H	N	ν(C≡N)	ν(C–S)	S cm^2 mol^{-1}
(22)	(1)	44.1	3.85	25.4	43.4	3.65	25.3	2 116, 2 102 2 090, 2 078	*b*	59
(23)	(2)	45.8	4.30	23.6	45.9	4.30	23.8	2 120, 2 109 2 081, 2 071	*b*	69
(24)	(3)	47.5	4.70	22.5	48.1	4.85	22.4	2 114, 2 104 2 075, 2 061	818	64
(25)	(4)	45.7	4.20	23.5	45.9	4.30	23.8	2 117, 2 106 2 088, 2 072	812	*c*
(25)	(5)	47.7	4.75	21.9	48.1	4.85	22.4	2 126, 2 108 2 085, 2 073	825	62
(27)	(6)	50.2	5.40	20.6	50.1	5.35	21.2	2 124br 2 099, 2 088	*b*	*c*
(28)	(7)	50.1	5.35	21.2	50.1	5.35	21.2	2 103, 2 092 2 073, 2 060	811	56

[a] For 10^{-3} mol dm^{-3} solutions in water at 22 °C. [b] No band clearly resolved. [c] Too insoluble.

given in Table 5. The conductivities obtained, where solubilities permit, are between the values expected for a 1 : 1 electrolyte and a non-electrolyte.[10] Since the electronic-spectral and magnetic properties of the complex are consistent with six-co-ordinate Ni^{II} (see below), it appears that some dissociation is occurring in aqueous solution. The frequency of the ν(C–S) absorption again indicates the presence of *N*-bonded thiocyanate groups.[14] The solid-state i.r. spectra all showed two groups of split bands in the ν(C≡N) region analogous to those observed for complex (15). Again, the implication appears to be that both *cis*-α and *cis*-β forms of the complex are present.

TABLE 6

Spectral (in cm^{-1}, ±1%) [a] and magnetic data for complexes of the type



Complex	R¹	R²	$^3A_{2g}\rightarrow{}^3T_{2g}$ ($10Dq$, ν_1)	$^3A_{2g}\rightarrow{}^1E_g$	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (ν_2)	$^3A_{2g}\rightarrow{}^1T_{2g}$	ν_2/ν_1	$\mu_{eff.}$ [b] B.M.
(22)	Me	H	10 270	12 280	18 080	20 200	1.76	3.14
(23)	Et	H	10 120	12 350	17 420	19 880	1.72	3.11
(24)	Pr	H	10 200	12 270	18 050	19 230	1.77	3 01
(25)	Me	Me	9 350	12 390	15 700	19 080	1.68	3.25
(26)	Et	Me	9 430		15 840	19 270	1.68	3.27
(27)	Et	Et	9 220		15 850	19 680	1.72	3.28
(28)	Pr	Me	9 400		15 770	19 190	1.68	3.25

[a] Solid-state data. [b] At 22 °C.

The nickel(II) complexes (22) — (28) all exhibited electronic solid-state spectra which approximate those expected of a regular octahedral complex. Details are given in Table 6. An approximate evaluation of $10Dq$ from the $3A_{2g}\rightarrow{}^3T_{2g}$ frequency shows the same trend in ligand-field strengths as that shown by the perchlorate salts of these complexes.[1] That is, with the ligands derived from ketones producing fields of the order of 1 000 cm^{-1} less than those produced by the less internally strained dihydrazones derived from aldehydes. The magnetic moments shown by (22) — (28) (Table 6) are also consistent with the octahedral nickel(II) formulation and show a departure from the spin-only value of 2.83 B.M. which is in accordance with the values of $10Dq$ determined above.*

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian HA-100 spectrometer using internal $SiMe_4$ as lock. Infrared spectra were determined as Nujol mulls using a Perkin-Elmer 237 spectrometer. Conductance data were obtained using a Wayne–Kerr universal bridge. Magnetic moments were measured on a Newport Gouy balance and are corrected for ligand and inner-core diamagnetism using Pascal's constants.[11] Electronic spectra were recorded on a Unicam SP 700A ultraviolet and visible spectrometer. Microanalyses were by the University Chemical Laboratory Microanalytical Department.

Di-isothiocyanatobis(pyridine)zinc(II) and di-isothiocyanatotetrakis(pyridine)nickel(II) were prepared by standard procedures.[12]

6,6'-Dihydrazino-2,2'-bipyridylzinc(II) *Perchlorate Complexes*, (8)—(14).—The appropriate dihydrazone ligand, (1)—(7) (1 mmol), was dissolved in methanol (20 cm^3) and heated under reflux under aerobic conditions for 15 min. Hexa-aquazinc(II) perchlorate (1 mmol) in methanol (5 cm^3) was then added and the solution was refluxed for another 10 min. The solution was then filtered and diethyl ether was added until the solution became cloudy, whereupon it was allowed to stand in the refrigerator overnight. The pale yellow crystals which formed were separated by filtration and required no further purification. In each case the yield was greater than 95%.

[*6,6'-Dihydrazino-2,2'-bipyridyl*]*di-isothiocyanatozinc*(II) *Complexes*, (15)—(21).—Di-isothiocyanatobis(pyridine)-zinc(II) (1 mmol) was suspended in refluxing methanol. The appropriate dihydrazone ligand, (1)—(7) (1 mmol), was added, and the suspension was heated under reflux for 15 min. The precipitated crystals were collected by filtration and washed with methanol (2 × 10 cm^3) to give the pure complex. In each case the yield was greater than 95%.

[*6,6'-Dihydrazino-2,2'-bipyridyl*]*di-isothiocyanatonickel* (II), (22)—(28).—Di-isothiocyanatotetrakis(pyridine)-nickel(II) (1 mmol) was suspended in refluxing methanol, the appropriate dihydrazone, (1)—(7), was added, and the suspension was heated under reflux for 15 min. In the case

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* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

[10] F. Basolo, 'The Chemistry of Co-ordination Compounds,' ed. J. C. Bailar, Reinhold, New York, 1956, p. 115.

[11] B. N. Figgis and J. Lewis, 'Modern Co-ordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, p. 400.

[12] G. B. Kauffman, R. A. Albers, and F. L. Harlan, *Inorg. Synth.*, 1970, **12**, 251.

of the symmetrical derivatives, (25) and (27), the product precipitated and was isolated by filtration and purified by washing with methanol (2×10 cm^3). In the other cases the product remained in solution and the solution was filtered and to it was added diethyl ether which precipitated the product. The product was then collected by filtration and washed with methanol to yield the pure complex. Yields were generally better than 80%.

[6/144 *Received*, 22*nd January*, 1976]