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THE GEOMETRY OF PENTACOORDINATE COMPLEXES

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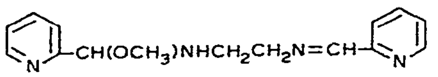
CONTENTS

ABBREVIATIONS

bpe,MeOH	methylated *N,N'*-bis(2-pyridylmethylene)ethane-1,2-diamine
biq	2,2'-biquinoline
catec	catecholate
5Cl-Salen-NEt$_2$	*N*-β-diethylaminoethyl-5-chlorosalicylaldiminate
dimim	1,2-dimethylimidazole
dmp	2,9-dimethyl-1,10-phenanthroline
Etphos	9-ethyl-9-phosphafluorene; 5-ethyl-5H-dibenzophosphole
H-Salen-NR$_2$	*N*-β-di-R-aminoethylsalicylaldiminate
H-Sal-MeDPT	bis(salicylaldiminotrimethylene)methylamine; bis(salicylidene-γ-iminopropyl)-methylamine
H-Sal-NMe	*N*-methylsalicylaldiminate
Me$_2$dpma	6,6'-dimethyldi-(2-pyridylmethyl)amine
Mephos	9-methyl-9-phosphafluorene; 5-methyl-5H-dibenzophosphole
paphy	pyridine-2-aldehyde-2'-pyridylhydrazone
Phisophos	2-phenylisophosphindoline
picox	2-picoline-*N*-oxide
QP	tris(*o*-diphenylphosphinophenly)phosphine
tda	tris(2-diphenylphosphinoethyl)-amine, N[CH$_2$CH$_2$P(C$_6$H$_5$)$_2$]$_3$
tepen	*N,N,N'*-tris[2-(2'-pyridyl)ethyl] 1,2-diamine
terpyridine	2,2',2''-terpyridine



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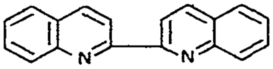

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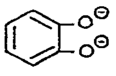

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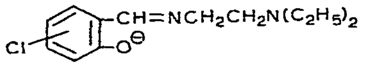
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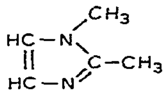
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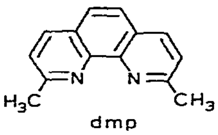
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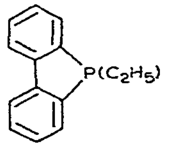
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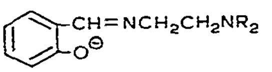
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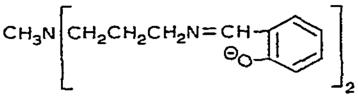
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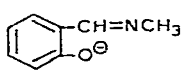
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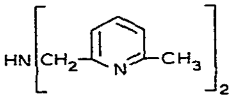
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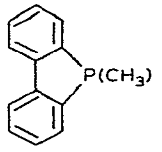
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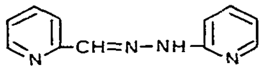
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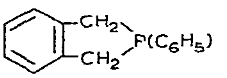
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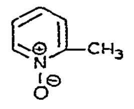
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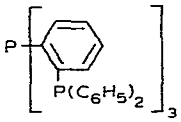
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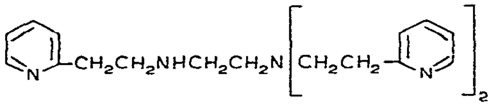
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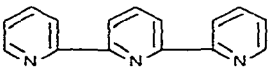
terpyridine

A. INTRODUCTION

Many reviews on pentacoordination, e.g. Ibers (1965)[1], Muetterties and Schunn (1966)[2], Blake et al. (1967)[3], Sacconi (1968)[4] and Chadwick et al. (1968)[5], are already available. Some more recent reviews by Orioli[6] and Sacconi et al.[7] have been published in this journal. This paper does not intend to duplicate the material covered in these reviews. It will, we hope, shed new light and present other aspects of pentacoordination with particular reference to those complexes with intermediate geometries. We shall advance reasons why these geometries are sometimes preferred to those which are more regular.

One of the most important requirements for the formation of a pentacoordinate transition metal complex is that the size and disposition of the coordinating ligands are such that only five donor atoms are allowed to approach the central metal ion closely. It has been shown that the stereochemical arrangement of these donor atoms may be based upon a trigonal bipyramid or a square pyramid; pentagonal planar or pentagonal pyramidal arrangements have been considered to be unlikely on steric grounds[8].

Sometimes a difficulty arises in the definition of the stereochemistry of a complex based upon a square pyramid. In solution there is the likelihood that a solvent molecule will bond to the metal ion in the sixth coordination site. In the solid state an atom, sometimes a hydrogen atom[9,10], of a nearby chelate might be found in this sixth site but at a greater distance from the metal ion than the other donor atoms; these "quasi-octahedral" (5 + 1) arrangements include many copper(II) complexes.

In general, however, a more serious difficulty arises in the definition of those stereochemistries which are found to be intermediate between trigonal bipyramidal (D_{3h}) and square pyramidal (C_{4v}) geometries. These two idealised geometries are rarely found in practice and compounds with so-called "trigonal bipyramidal" or "square pyramidal" geometries may often be severely distorted from the idealised forms. A problem associated with this is that often the geometry of a complex is described as being of one form when using other criteria it is much closer to the other form. Attempts to overcome this problem have been made by Zemann[11] who proposed in 1963 a simple R factor test, $\Sigma_1^{10}\ |\angle\mathrm{LML(theor.)}-\angle\mathrm{LML(exp.)}|/\Sigma_1^{10}\ |\angle\mathrm{LML(theor.)}|$, for the ten ligand–metal–ligand angles. The poor response to this proposal possibly reflects the tendency of researchers to use a subjective judgment on this matter.

In their review Muetterties and Schunn[2] drew attention to the striking resemblance of the two idealised forms when the view down a C_2 axis of a trigonal bipyramid is compared with that down the C_4 axis of a square pyramid (Fig. 1). They also referred to the stereochemical non-rigidity of these forms, pointing out that there may be a very fast or very slow interconversion rate between the two forms with the interconversion proceeding through an energy barrier. They pointed out that the difference in energy between the two idealised geometries is very small for most electronic configurations and that the trigonal bipyramidal geometry might prove to be the most common ground state except in cases where there may be some ligand stabilisation of the square pyramidal geometry.

As many complexes have been observed by X-ray diffraction methods to possess geometries intermediate between the two idealised forms it is proposed, in the light of some simple energy calculations described in Sect. C, that these intermediate geometries need to be considered when predicting the geometry which five donor atoms adopt when coor-

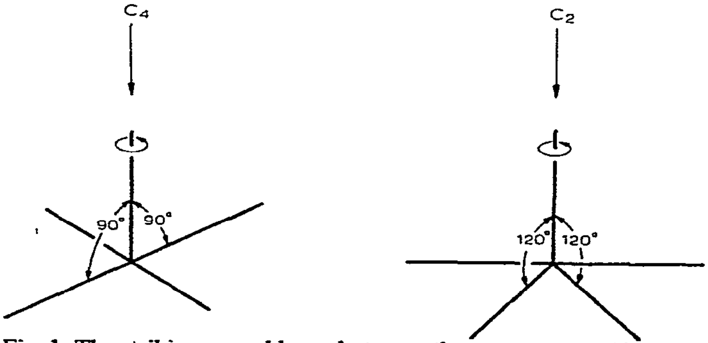

Fig. 1. The striking resemblance between the square pyramid and the trigonal bipyramid.

dinating to a metal atom.

B. THE CHOICE OF PENTACOORDINATE GEOMETRY

(i) Factors governing the choice

There have been various attempts to account for the square pyramidal and trigonal bipyramidal geometries. One early attempt predicted that square pyramidal coordination would be favoured by dsp^3 hybridisation and that trigonal bipyramidal coordination would be favoured by sp^3d hybridisation[12].

The problem of the relative stability of the different forms has been treated by Zemann for five similar ligands equidistant from the metal ion[11]. On the basis of charge repulsion Zemann demonstrated that the trigonal bipyramid is more stable than the square pyramid. This treatment succeeded in showing that a square pyramidal configuration was likely to be distorted, with the metal ion displaced from the basal plane and towards the apical atom of the square pyramid. Such a distortion (leading to apical-to-basal bond angles of 104.1° and basal-to-basal bond angles of 86.6° and 151.9°) was found to be much more stable than a regular square pyramid, assuming a weak ligand field, and only slightly less stable than a trigonal bipyramid[11].

These findings of Zemann were in general agreement with those of Sidgwick and Powell. These latter workers predicted on the basis of their electron pair repulsion theory that a trigonal bipyramidal configuration would be the more stable geometry for non-transition metal complexes[13].

Gillespie and Nyholm[14] extended the valence-shell electron-pair repulsion theory to include transition metal complexes by consideration of the interaction between bonding electron-pairs and the non-bonding d-electrons of the metal atom. Five covalent complexes with d^0, d^{10}, and d^5 (spin-free) configurations should have trigonal bipyramidal geometry because a spherically symmetric d-shell has no effect on the arrangement of the valence-shell electron-pairs. Ligand field calculations[15], treating the ligands as point negative charges, show that in every case from d^1 to d^9 the energy of the d-electrons is less for the square pyramidal than for the trigonal bipyramidal configuration. However, it is known that the interactions between the bonding electron-pairs themselves favour the trigonal bipyramidal arrangement, so that when the interactions between the bonding electron pairs are more important than their interactions with the non-bonding d-electrons, as is probably the case in complexes of high "covalent" character, trigonal bipyramidal geometry is favoured. If the predominant interaction is that between the bonding electron pairs and the non-bonding d-electrons, which is probably the situation in complexes of essentially "ionic" bonding, then a square pyramidal complex is to be expected. When all the interactions are comparable, structures of intermediate geometry might be expected. Interactions between bonding electron-pairs and the d-shell are likely to be weak when the number of d-electrons is small, i.e. for d^1, d^2, and possibly d^3 configurations. It has been reported by Ciampolini[16] that when the apical-to-basal bond angle, ∠LML, increases from

100 to 105° the difference in CFSE between the two geometries is substantially reduced, so much so that the trigonal bipyramidal geometry is more stable for high-spin d^4, d^9 and low-spin d^8 configurations.

A recent attempt by Furlani[17] to rationalise the electronic spectra of pentacoordinate complexes with ligand field theory has been made. In this treatment the effect of π-bonding is thoroughly discussed; π-bonding tends to stabilise the regular square pyramidal geometry, with an apical-to-basal bond angle of 90°, because all ligands can then take part in π-bonding with full efficiency. This stabilisation is most obvious when interligand π conjugation is possible. It is interesting to note that this appears to contradict the generalisation of Gillespie cited above, as π-bonding ligands might be considered to produce bonds more covalent in nature than those produced by ligands without this capacity for accepting or donating π-bonding electrons. It is for this reason that Furlani has stated that coordination forces which are "mainly electrostatic or σ-covalent" in nature will tend to stabilise the trigonal bipyramidal geometry.

A very important factor affecting the arrangement of donor atoms in a pentacoordinate complex is that of chelate conformation. Lions, in reporting the design[18] of quinquedentate chelates, gives some examples of chelates whose conformations might be expected to enforce square pyramidal or trigonal bipyramidal geometries. Allied to this factor is that of steric influence between different ligands or different parts of the same chelate.

In summarising the factors controlling the stereochemistry of pentacoordinate complexes, it is postulated that π-bonding and the CFSE will stabilise the "regular" square pyramidal geometry. If the ligand–ligand repulsion or chelate strain forces are sufficiently great, the basal bonds may be depressed to give a "distorted" square pyramidal, a trigonal bipyramidal or an intermediate type of geometry. In these geometries four basal bonds, two basal bonds and one basal bond respectively are depressed away from the apical atom of the regular square pyramid (Fig. 2).

If the stereochemistry of the metal atom in the intermediate geometries is viewed as that based on the trigonal bipyramidal arrangement then the atoms α, β and δ defined in Fig. 2 constitute the trigonal plane with the atoms γ and ϵ in the axial positions. Alternatively, if the stereochemistry is described as square pyramidal, it is often difficult to define a basal plane because one of the atoms, δ, is considerably depressed from the plane in the direction away from the apical atom, α. Table 1 lists many compounds which can be considered as intermediate complexes of this type.

Which of the above geometries is favoured depends markedly upon the fine balance of forces provided by the CFSE (and hence the type and oxidation state of the metal atom), the nature of the metal-to-ligand bond (covalent versus ionic bonding; π-bonding) and the various inter- and intraligand steric strains and repulsions. Indeed, the energy differences are so small that on some occasions the geometry is determined by crystal packing forces.

(ii) Examples illustrating the governing factors

(a) Crystal packing forces

TABLE 1

Pentacoordinate complexes with distorted geometries

Compound No.	Complex[a]	Structure No.	Angles[b]					Ref.
			Triangular plane			Axial to axial	Others	
			$\beta\delta$	$\alpha\beta$	$\alpha\delta$	$\gamma\epsilon$		
1	$[Cu(NH_2CH(COO)CH(Me)(Et))_2H_2O]$		163	85	112	175	84–99	19
2	$[Pd(Phisophos)_3Br_2]$		160[c]	92	105		84–97	20
3	$[Au^{III}(biq)Cl_3]$		160[c]	80[c]	120[c]			21
4	$[\beta\text{-}Co(paphy)Cl_2]$		157	94	110	149[c]	74–102	22
5	$[Cl(dmp)NiCl_2Ni(dmp)Cl].CHCl_3$		157	82	121	162	82–100	23
6	$[Cu(dmp)Cl_2H_2O]$		156	101	104	171	80–106	24
7	$[Ni(5Cl\text{-}Salen\text{-}NEt_2)_2]$		154	100	105	163	82–105	25
8	$[Ni(triarsine)Br_2]$	XVII	154	95	111	175	88–93	26
9	$[Cu(OC(Me)CHC(Me)NCH_2CH_2O)]_4$		153	81	121	178		27
10	$[Zn(acetylacetonate)_2H_2O]$		150	105	105	162	85–100	28
11	$[NiLBr_2]$, where L is $o\text{-}MeO.C_6H_4.CH_2NH(CH_2)_3NHEt$		150	101	107	175	85–97	9
12	$[Co(terpyridine)Cl_2]$	XVIII	150	99	111	147	74–102	29
13	$[Ni(Me_2dpma)Br_2]$		149	99	112	164	81–94	30
14	$[Cu(bpe,MeOH)Br]ClO_4$		146	102	111	160	79–101	31
15	$[Ni(dmp)(S_2P(OMe)_2)_2]$		146	83	130	166	82–100	32
16	$[Ni(H\text{-}Salen\text{-}NEt_2)(catec)]_2$		145	98	117	178		33
17	$[Cd(SC(NH_2)_2)_3(OSO_3)]_2$		145	97	115	156	82–113	34
18	$[Cd(S_2CN(Et)_2)_2]_2$	VII	145	106	108	159	68–110	35
19	One form of $\beta\text{-}Zn_3(PO_4)_2$		144	102	111	132	77–122	36
20	$[Zn(terpyridine)Cl_2]$	XIX	143	105	112	145	73–102	37
21	$[Ni(H\text{-}Sal\text{-}MeDPT)]$		142	105	113			38
22	$[Cu(1,10\text{-}phenanthroline)_2H_2O](ClO_4)_2$							39

23	One form of Ni in $[Cr(en)_3][Ni(CN)_5].1\frac{1}{2}H_2O$	II	141	107	111	173	85–94	40
24	$[Ni(P(OEt)_2Ph)_3(CN)_2]$		141[c]	107[c]	111[c]			41
25	$[Ni(Mephos)_3(CN)_2].\frac{1}{3}H_2O$	XIV	140	108	112	161	86–101	42
26	$[Cu(H\text{-}Salen\text{-}NMe_2)_2]$		140	92	127	169	76–94	43
27	$[Cu(dimim)_3Cl_2]$		138	104	118	177	88–92	44
28	$[Zn(S_2CN(Et)_2)_2]_2$	VI	138	108	112	160	70–107	45
29	$[Co(PHPh_2)_3Br_2]$	XXV	136	98	126	176	87–91	46
30	$[Cu(pyridine\text{-}N\text{-}oxide)_2Br_2]_2$	XII	135[c]	108[c]	119			47
31	$[Co(MeN(CH_2CH_2NMe_2)_2)Cl_2]$		135	107	113	162	78–104	48
32	$[Co(QP)Cl]BPh_4$	XXIII	134	109	113	171	85–99	49
33	Ni^{III} in $[Ni^{III}(PPhMe_2)_2Br_3]\cdot.\frac{1}{2}[Ni^{II}(PPhMe_2)_2Br_2].C_6H_6$	XXXI	133	111	117	179		50
34	$[Ni(Mephos)_3(CN)_2].CH_3OH$	XV	133	111	116	176	87–94	42
35	Cu_2OSO_4, dolerophanite		133	111	111			51
36	$[Ni(PHPh_2)_3I_2]$	XXIV	133	105	123	174	87–93	46
37	One form of Al in a bromoaluminosiloxane		132	114	114	158	74–102	52
38	$[Co(picox)_5](ClO_4)_2$	XXVIII	130	114	115	173		53
39	$[Cu(N(CH_2CH_2NH_2)_3)NCS]NCS$		130	113	114			54
40	$[Co^{I}(CNCH_3)_5]^+$	XXVII	128	116	116	180	89–91	55
41	$[Co(HN(CH_2CH_2NEt_2)_2)Cl_2]$		127	106	120	173	80–102	56
42	$[Ni(Etphos)_3(CN)_2]$	XIII	126	112	122	177	88–93	42
43	$[Cu(2,2'\text{-}bipyridine)_2I]I$	XXXII	124	114	122	178[c]		57
44	$[Cr(NMe_3)_2Cl_3]$	XXX	124	112	124			58
45	$[Ti(NMe_3)_2Br_3]$	XXIX	121	117	121			58

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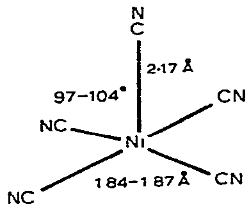
[a] All metal atoms are M^{II} unless specified.

[b] The labelling of the bond angles refers to Fig. 2(c).

[c] Estimated or assumed value.



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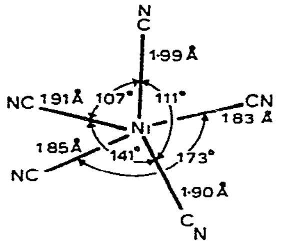

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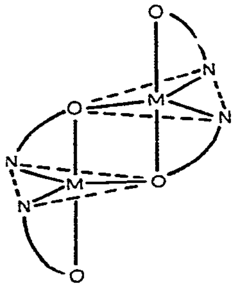

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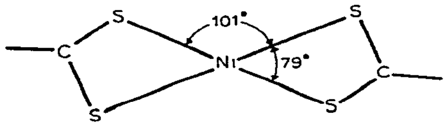

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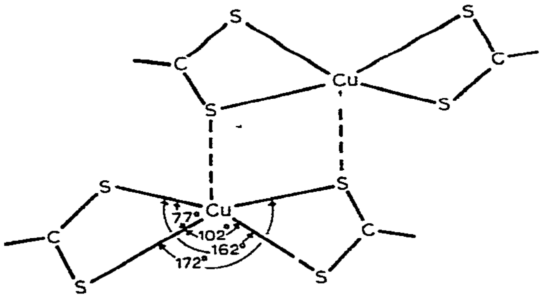

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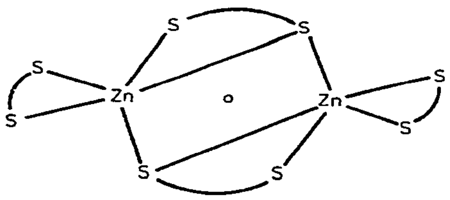

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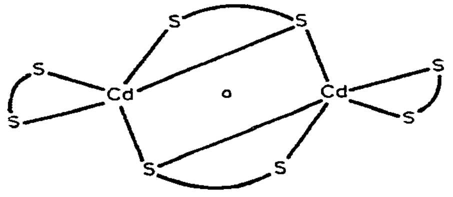


VII

Structures: I and II, stereochemical forms of the $[Ni(CN)_5]^{3-}$ anion. III, $M_2(H\text{-}Sal\text{-}NMe)_4$; M = Ni or Zn. IV, $Ni(S_2CNEt_2)_2$. V, $Cu_2(S_2CNEt_2)_4$. VI, $Zn_2(S_2CNEt_2)_4$. VII, $Cd_2(S_2CNEt_2)_4$.

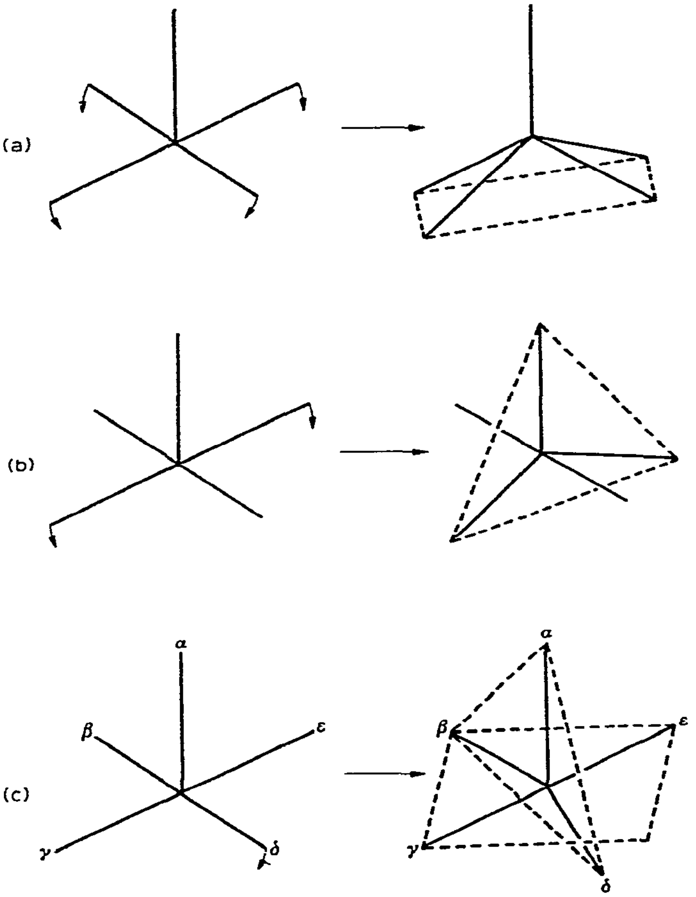
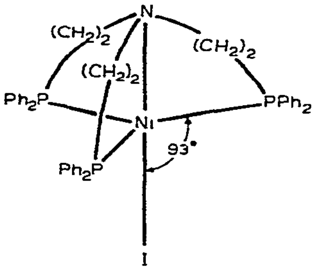
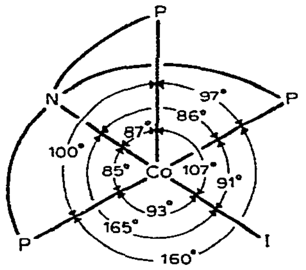


Fig. 2. The distortions required to obtain the distorted square pyramidal geometry (a); the trigonal bipyramidal geometry (b), and the intermediate geometry (c) from a regular square pyramid.

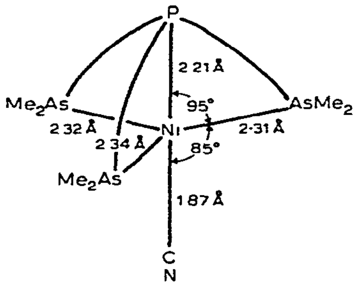
Two examples of a geometry determined by crystal packing forces are provivided by $[Cr(en)_3]$ $[Ni(CN)_5] \cdot 1\frac{1}{2}H_2O$ (ref. 40) and tetrakis(*N*-methylsalicylaldiminato)-dinickel(II), $[Ni_2(H\text{-}Sal{-}NMe)_4]$ (ref. 59). In the former compound two stereochemical forms of pentacoordinate nickel(II) are found. In one form the nickel has a square pyramidal stereochemistry with apical-to-basal bond angles of 97 to 104°, I; this form is apparently stabilised by π-conjugation among the basal ligands. The second form has an intermediate stereochemistry, II (No. 23 in Table 1), which is a most surprising observation for five similar monodentate ligands; it is assumed that the weak hydrogen bonding in the crystal



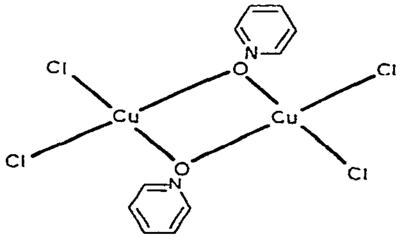
VIII



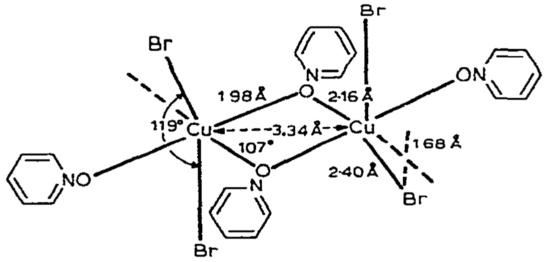
IX



X



XI



XII

Structures: VIII, [Ni(tda)I]$^+$. IX, [Co(tda)I]$^+$. X, [NiP(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_3$CN]$^+$. XI, [(pyridine-*N*-oxide)$_2$CuCl$_2$]$_2$. XII, [(pyridine-*N*-oxide)$_2$CuBr$_2$]$_2$.

causes a sterochemical conversion from the square pyramidal form to another stable (or metastable) geometry[40]. The second compound has been crystallised in three modifications. The α and β forms are diamagnetic, monomeric and *trans* square planar complexes. These dissolve in the crystal lattice of the analogous zinc complex and in so doing mimic its trigonal bipyramidal structure, III, and become paramagnetic binuclear compounds[59]. This demonstrates that the host lattice can provide enough energy to cause the guest complex to convert from the stereochemistry in which it normally crystallises to that of the host[60].

(b) The metal ion and CFSE

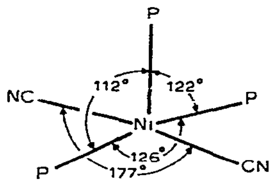
The influence of the metal ion on the geometry can be seen in complexes containing diethyldithiocarbamate chelates. It is found that the nickel(II) complex IV has a square planar stereochemistry[61], the copper(II) complex V has distorted square pyramidal stereochemistry[62] and the zinc(II) complex VI (No. 28 in Table 1) has an intermediate-type stereochemistry[45]; it should be noted here that the cadmium(II) complex VII (No. 18 in Table 1) has an intermediate geometry[35] very similar to that of the zinc(II) complex.

The cation of the diamagnetic compound [Ni(tda)I]I, where tda is the tris(2-diphenylphosphinoethyl)amine chelate, is found to be a regular trigonal bipyramid, VIII[63] whereas that of [Co(tda)I]I is found to be a square pyramid, IX[64]. This is in agreement with the calculated values of the CFSE; the square pyramidal C_{4v} symmetry is found to be 7.4% more stable for cobalt(II) and 2.7% less stable for nickel(II) than the trigonal bipyramidal D_{3h} symmetry[16]. It is interesting to note that solutions of [Co(tda)I]I appear to equilibrate between the low-spin square pyramidal and high-spin trigonal bipyramidal stereochemistries with the proportion of the latter increasing with increasing temperatures. This observation suggests that the interconversion energy is very small and that the ground-state geometry for the $[Co(tda)I]^+$ cation is low-spin square pyramidal[65].

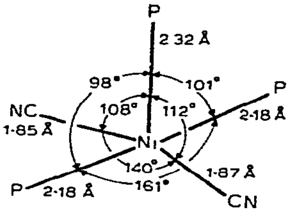
(c) Interligand repulsion

The influence of interligand repulsion on the stereochemistry of a complex is apparent in the following examples. The complex cation of the low-spin compound $[Ni(P(CH_2CH_2CH_2AsMe_2)_3)Z]ClO_4$ has a trigonal bipyramidal geometry X when Z is a cyanide ion. However, the complex ion with Z a bromide ion is not isostructural with that of the cyanide; it has been reported as a distorted square pyramid[66]. The larger radius of the bromide ion seems to cause a greater repulsion between Z and the methyl groups of the tripod chelate, forcing the cation to adopt another geometry. Also, the different π-bonding characteristics of the Br^- and CN^- ligands must undoubtedly have a significant effect.

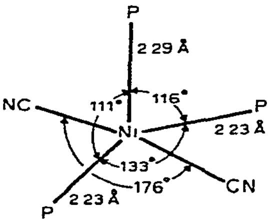
For the complexes $[(\text{pyridine-}N\text{-oxide})_2CuZ_2]_2$, where Z is chloride or bromide, the difference in size between a chloride and a bromide ion is apparently enough to affect not only the stereochemistry of the metal ion but also the relative positioning of the ligands. In the chloride complex the copper atom is surrounded by two terminal chlorine and two bridging oxygen atoms forming the base, and one oxygen atom forming the apex of a



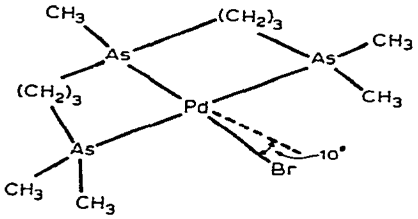
XIII



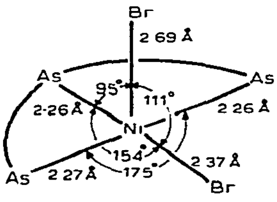
XIV



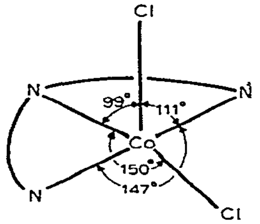
XV



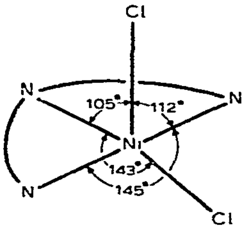
XVI



XVII



XVIII



XIX

Structures: XIII, [Ni(Etphos)$_3$(CN)$_2$]; Ni – CN = 1.82 – 1.85 Å; Ni – P = 2.24 – 2.27 Å. XIV, [Ni(Mephos)$_3$(CN)$_2$].$^1/_3$H$_2$O; Ni – CN = 1.85 – 1.87 Å; Ni – P = 2.18 – 2.32 Å. XV, [Ni(Mephos)$_3$(CN)$_2$].CH$_3$OH; Ni – CN = 1.86 – 1.87 Å; Ni – P = 2.22 – 2.29 Å. XVI, [Pd(triarsine)Br]$^+$. XVII, [Ni(triarsine)Br$_2$]. XVIII, [Co(terpyridine)Cl$_2$]. XIX, [Ni(terpyridine)Cl$_2$].

square pyramidal arrangement, XI. On the other hand, the bromide complex XII (No. 30 in Table 1) has an intermediate-type structure where one terminal and two bridging oxygen atoms are coplanar with the copper atom; one bromide atom is in an apical position and the other is depressed 1.68 Å below the basal plane[47].

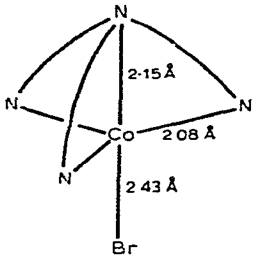
The different geometries of the [Ni(Mephos)$_3$(CN)$_2$] and [Ni(Etphos)$_3$(CN)$_2$] compounds provide an interesting illustration of the effect of using different ligands. While a distorted trigonal bipyramidal geometry is observed for the Etphos compound XIII (No. 42 in Table 1), two different forms of the Mephos compound, an intermediate geometry XIV (No. 25 in Table 1) and a distorted trigonal bipyramidal geometry XV (No. 34 in Table 1) can be isolated[42]. Crystal packing forces also appear to affect the choice of geometry in the Mephos compound as the resulting geometry is dependent upon the method of recrystallisation; these two forms, XIV and XV, are believed to contain water and methanol molecules, respectively, residing in lattice holes as molecules of crystallisation[42]. These observations suggest that for low spin d^8 configurations the difference in CFSE between the trigonal bipyramidal and the intermediate geometries is less than the difference in the ligand-to-ligand repulsion energies and any difference in lattice energies. It is very interesting to note here that it is the less bulky ligand which produces the intermediate geometry.

The effect of polydentate chelate conformation on the positioning of monodentate ligands is demonstrated in complexes containing the terdentate chelate of $Me_2As(CH_2)_3AsMe(CH_2)_3AsMe_2$, triarsine. The [Pd(triarsine)Br]$^+$ cation XVI is observed[26] to have a distorted square planar geometry with the Pd–Br bond depressed out of the square plane by an angle of about 10°. As no atom resides in the apical position normal to the square plane this distortion is seemingly caused by the steric influence between the terminal methyl groups of triarsine and the bromide ion. In the [Ni(triarsine)Br$_2$] complex XVII (No. 8 in Table 1), which has a bromide ion at the apex, the basal bromide ion is depressed about 20° out of the basal plane. This effect is consistent with an increase in the steric repulsion resulting from the decreased metal-to-ligand distance[26].

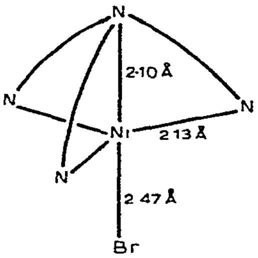
(d) Electronic distortion

Polydentate chelates may also be used to demonstrate the effect of electronic factors on the observed stereochemistry. An example of this is provided by two [M(2, 2′, 2″-terpyridine)Cl$_2$] compounds, XVIII and XIX. These compounds have intermediate-type geometries with the two chlorine atoms occupying two sites in the triangular plane of the grossly distorted trigonal bipyramid or, when viewed as a distorted square pyramid, occupying the apical and depressed ligand sites. The angles of the triangular plane appear to be dependent upon interactions between bonding and non-bonding electrons as the $\angle$ClMCl′, $\angle$ClMN and $\angle$Cl′MN bond angles of 111°, 150° and 99° respectively in the d^7 Co^{II} complex XVIII (No. 12 Table 1)[29] are quite different from those of 112°, 143° and 105° respectively in the d^{10} Zn^{II} complex XIX (No. 20 in Table 1)[37].

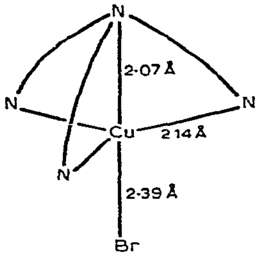
As a further example, the high-spin complex cations of the series of compounds [M(N(CH$_2$CH$_2$NMe$_2$)$_3$)Br]Br have trigonal bipyramidal geometries. Although the bond angles are very similar there are some marked differences in bond distances. For example,



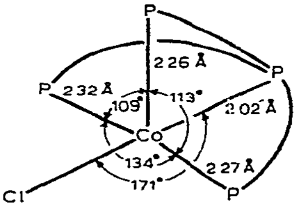
XX



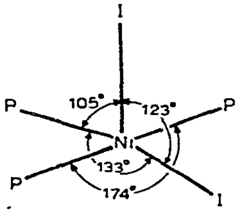
XXI



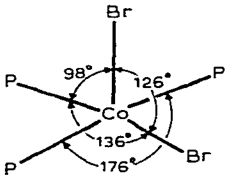
XXII



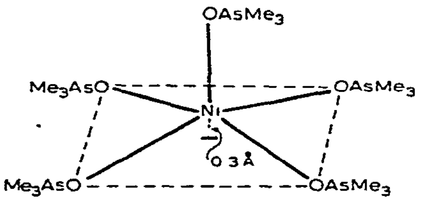
XXIII



XXIV



XXV



XXVI

Structures: XX, $[CoN(CH_2CH_2NMe_2)_3Br]^+$. XXI, $[NiN(CH_2CH_2NMe_2)_3Br]^+$. XXII, $[CuN(CH_2CH_2NMe_2)_3Br]^+$. XXIII, $[Co(QP)Cl]^+$. XXIV, $[Ni(PHPh_2)_3I_2]$. XXV, $[Co(PHPh_2)_3Br_2]$. XXVI, $[Ni(OAsMe_3)_5]^{2+}$; Ni–O = 1.95–2.02 Å.

the axial M–Br bond length has been observed as 2.431 Å for the d^7 Co^{II} complex XX[67], 2.467(2) Å for the d^8 Ni^{II} complex XXI[68] and 2.393(3) Å for the d^9 Cu^{II} complex XXII[68]; see Orioli[6]. On the other hand, the low-spin [Co(QP)Cl]$^+$ ion[49], where QP is tris-(*o*-diphenylphosphinophenyl)phosphine, has an intermediate-type geometry XXIII (No. 32 in Table 1); the three terminal phosphine groups occupy the coordination sites of the grossly distorted trigonal plane with ∠PCoP angles of 134°, 113° and 109°.

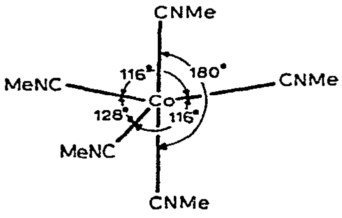
The distorted trigonal bipyramidal complexes of [Ni(HPPh$_2$)$_3$I$_2$], XXIV (No. 36 in Table 1), and [Co(HPPh$_2$)$_3$Br$_2$], XXV (No. 29 in Table 1) crystallise with the two halogen ligands occupying two of the three equatorial sites[46,69]. It is interesting to observe that, while the halogen–metal–halogen angle in these compounds is in the range of 123–126°, the other two angles in each of the trigonal planes are substantially different (98–105° compared with 133–136°). This considerable distortion might be attributed to the asymmetry of the phosphine ligands and partly to the asymmetry of the non-bonding *d* electrons.

Complexes of particular interest are those d^1 to d^9 complexes containing five identical ligands as these are most likely to provide experimental evidence for electronic distortions. Structures of crystals containing the ions [Mn(CO)$_5$]$^-$ (ref. 70), [Fe(CO)$_5$] (ref. 71), [Co^I(CNCH$_3$)$_5$]$^+$ (ref. 55), [Co(picox)$_5$]$^{2+}$ (ref. 53), [Ni(CN)$_5$]$^{3-}$(ref. 40), [Ni(OAsMe$_3$)$_5$]$^{2+}$ (ref. 72), [Ni(P(OCHCH$_2$)$_3$)$_5$]$^{2+}$ (ref. 73), [Pt(SnCl$_3$)$_5$]$^{3-}$ (ref. 74) and [CuCl$_5$]$^{3-}$ (ref. 75) have been reported. Two of these complexes do not have a trigonal bipyramidal geometry. These are the high-spin [Ni(OAsMe$_3$)$_5$]$^{2+}$ ion, a distorted square pyramid XXVI, and the low-spin [Ni(CN)$_5$]$^{3-}$ ion, the geometry of which has been described previously (I and II). Crystals containing the [Cu(NO$_2$)$_5$]$^{3-}$ ion have been subjected to a preliminary X-ray investigation[76].

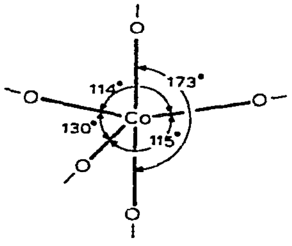
The [Co^I(CNCH$_3$)$_5$]$^+$ cation is observed to have significantly different angles (128.3°, 115.9° and 115.9°) in the trigonal plane of its trigonal bipyramidal geometry XXVII (No. 40 in Table 1)[55]; the [Co^{II}(picox)$_5$]$^{2+}$ cation has a very similar geometry XXVIII (No. 38 in Table 1)[53] with angles of 129.8°, 115.4° and 113.7°. This type of distortion has also been reported for the d^1 [Ti(NMe$_3$)$_2$Br$_3$], XXIX (No. 45 in Table 1)[58], and d^3 [Cr(NMe$_3$)$_2$Cl$_3$], XXX (No. 44 in Table 1)[58] complexes; a comparison of the angles in the trigonal planes of these *trans* trigonal bipyramidal complexes (117.5°, 2 × 121.2° and 111.6°, 2 × 124.2° respectively) clearly shows that the effect is probably due to an interaction between the bonding electron pairs and the non-bonding *d* electrons.

C. SOME ELECTROSTATIC CALCULATIONS ON AN INTERMEDIATE GEOMETRY[77]

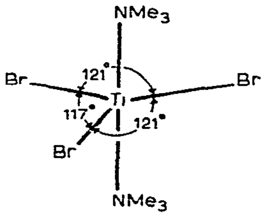
Because the intermediate geometries appear to possess energies similar to those of the trigonal bipyramidal and distorted square pyramidal geometries (see Sect. B(*ii*)) some simple calculations have been made and these are reported in this section. The chosen geometrical model, illustrated in Fig. 3, seemed particularly suitable in simulating the intermediate geometry observed in many of the complexes listed in Table 1.



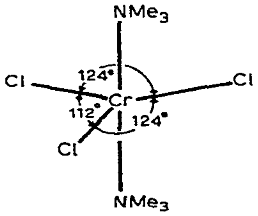
XXVII



XXVIII



XXIX



XXX

Structures: XXVII, $[Co(CNCH_3)_5]^+$. XXVIII, $[Co(picox)_5]^{2+}$. XXIX, $[Ti(NMe_3)_2Br_3]$. XXX, $[Cr(NMe_3)_2Cl_3]$.

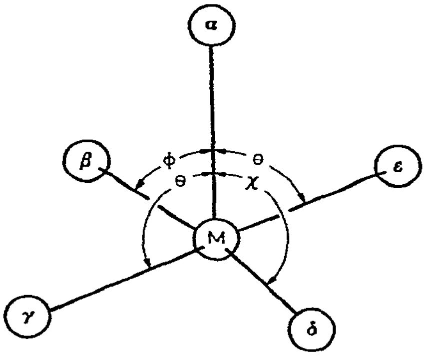


Fig. 3. The model used for the electrostatic calculations.

Some restrictions were placed upon the model. First, all five ligands were assumed to have an equivalent point charge and to lie at the same distance from the central metal atom, M. Secondly, the set of atoms in the grossly distorted trigonal plane, α, β, δ and M, were assumed to be always coplanar and, likewise, coplanarity was assumed for the atoms α, γ, ϵ and M. Finally, the angles between the apical ligand of the square pyramidal description, α, and the axial ligands of the trigonal bipyramidal description, γ and ϵ, were assumed to be equivalent.

The potential energy due to the interligand electrostatic repulsion was calculated from the expression

$$U \propto \sum_{i=1}^{10} x_i^{-1}$$

where x_i is one of the ten ligand–ligand distances[*]. The minimum value of this potential energy is reported in Fig. 4 for various combinations of θ and ϕ (defined in Fig. 3) and the value of χ at this minimum is also reported.

As can be seen from Fig. 4, curve A has a minimum potential energy of 6.475 units when the geometry is that of a regular trigonal bipyramid ($\theta = 90°$; $\phi = \chi = 120°$) and curve C has a minimum of 6.484 energy units when the geometry is that of a distorted square pyramid with all the apical-to-basal bond angles equal to 104.08°. As the repulsion between the ligands in a regular square pyramid was calculated to have a relative potential energy of 6.657 units, the findings of Zemann[11] (see p. 368) have been verified. Furthermore, the minimum potential energy of 6.479 units for curve B show that, while the intermediate geometry has slightly more interligand repulsion than a regular trigonal bipyramid, it can have less interligand repulsion than a distorted square pyramid.

It appears that, in cases where interligand repulsion or steric hindrance prevent the adoption of a trigonal bipyramidal geometry and where these two factors dominate over those

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[*] Relative to a metal–ligand distance of unity.

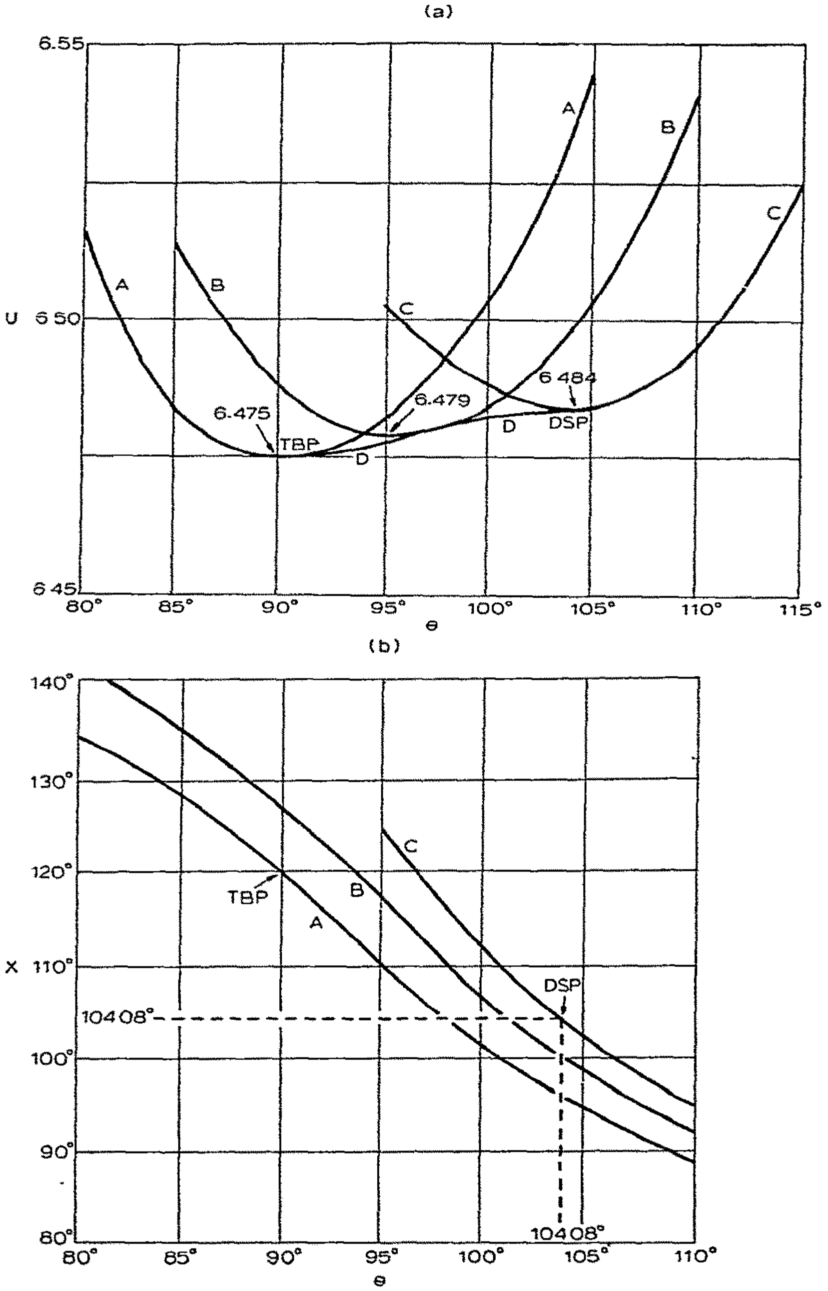
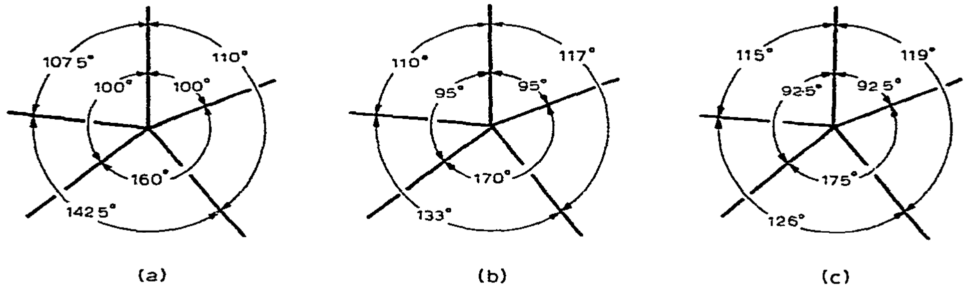


Fig. 4. The minimum potential energy (a), and the value of χ corresponding to this minimum potential energy for defined values of θ and ϕ (b). Curve A, $\phi = \theta + 30°$; curve B, $\phi = \theta + 15°$; curve C, $\phi = \theta$; curve D, see text (p. 383). TBP: trigonal bipyramid; DSP: distorted square pyramid.



(a) (b) (c)

Fig. 5. The geometry of the complex with minimal interligand repulsion when the angles of the complex are related by $\phi = \theta + 7.5°$ ($U = 6.482$ units) (a); $\phi = \theta + 15°$ ($U = 6.479$ units) (b), and $\phi = \theta + 22.5°$ ($U = 6.476$ units).

factors which generally favour the formation of square pyramidal complexes (namely π-bonding and CFSE), the geometry of the complex is likely to be intermediate between the two idealised forms. In addition, the ligand–metal–ligand angles in a complex are likely to be such that the potential energy lies as close as possible to curve D in Fig. 4. Some five-coordinate geometries with their potential energies lying on curve D are illustrated in Fig. 5.

D. RATIONALISATION OF CALCULATIONS WITH OBSERVED STRUCTURES

In this section an attempt is made to rationalise the observed geometries of several pentacoordinate complexes in terms of the simple energy calculations described in Sect. C.

Those complexes with an intermediate geometry similar to the calculated model illustrated in Fig. 5(a) are Nos. 14 and 19–25 in Table 1. The observed geometries of these complexes lend substantial support to the conclusions advanced in Sect. C, as the three complexes with only monodentate ligands, Nos. 23–25 in Table 1, have geometries very similar to the calculated model (Fig. 5(a)); two of these complexes are worth discussing in more detail.

It is interesting to note that, while the bond angles in the distorted triangular plane of the intermediate-type pentacyanonickelate(II) complex II (No. 23 in Table 1) are almost the same as those of the calculated model, the observed axial–axial bond angle of 173° is significantly greater than that of 160° for the calculated model (Fig. 5(a)). As the axial Ni–CN bond distances of 1.83 and 1.85 Å are significantly shorter than the other three Ni–CN bond distances from 1.90 to 1.99 Å, it might be expected that the indicated π-conjugation involving these two axial ligands would cause the axial–axial bond angle to approach 180°.

The geometry in the low-spin, intermediate-type dicyanotris(5-methyl-5H-dibenzophosphole)nickel(II) molecule XIV (No. 25 in Table 1) is almost identical with that of the calculated model illustrated in Fig. 5(a). The two Ni–P bond distances of 2.18 Å in the distorted square plane of this complex are substantially shorter than the Ni–P distances of

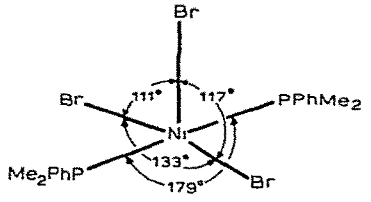
2.22–2.29 Å observed in its grossly distorted trigonal bipyramidal allogen XV (No. 34 in Table 1) and its Etphos analogue XIII (No. 42 in Table 1). It seems that the smaller interligand repulsion between the less bulky Mephos ligands permits the Mephos ligand to approach the nickel atom a little more closely (compare XIII with XV) than the Etphos ligand. This increased bond strength appears to overshadow the effect of CFSE which would have tended to stabilise the trigonal bipyramidal geometry[16]. The other Ni–P bond distance of 2.32 Å in complex XIV is consistent with other low-spin square pyramidal d^8 complexes; differences between basal and apical bond distances in low-spin d^8 square pyramidal complexes have been observed as 0.1 Å for Ni–As bonds[78], 0.3 Å for Ni–CN bonds[40], 0.4 Å for Ni–Br bonds[10], and 0.6 Å for Ni–S bonds[79].

Complexes 30–34 and 36 in Table 1 have an intermediate geometry similar to the calculated model illustrated in Fig. 5(b). The quadridentate chelate chlorotris(*o*-diphenylphosphinophenyl)phosphinecobalt(II) tetraphenylborate XXIII (No. 32 in Table 1) might have been expected to force a trigonal bipyramidal environment about the cobalt(II) atom. The grossly distorted trigonal plane of the intermediate geometry about the cobalt atom, with ∠PCoP angles of 134°, 113° and 109°, can be explained as a compromise between the preference of a high-spin d^7 complex for adopting a square pyramidal geometry in order to achieve a greater CFSE[16] and the preference of the quadridentate chelate for enforcing a trigonal bipyramidal geometry (due to the sp^3 hybridisation of the central phosphorus atom and the intraligand repulsion between its diphenylphosphino moieties). One can discount the possibility that the symmetrical tetraphenylborate ion influences the geometry of the complex.

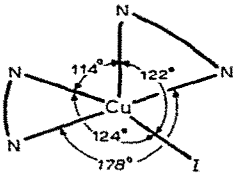
There is a remarkable similarity between one of the forms of $[Ni(Mephos)_3(CN)_2]$, XV (No. 34 in Table 1) and the five-coordinate, low-spin Ni^{III} species in $[Ni^{III}(PPhMe_2)_2Br_3] . \frac{1}{2} [Ni^{II}(PPhMe_2)Br_2] . C_6H_6$, XXXI (No. 33 in Table 1). In each case the three like ligands occupy the three sites of the grossly distorted trigonal plane; not only are the three angles in this plane identical to those in the calculated model illustrated in Fig. 5(b) but also the three nickel-to-ligand distances of this plane in each of the two complexes show a distinct similarity. The observed lengthening of the nickel–apical donor atom bonds can be explained in terms of repulsion from the d_{z^2} electrons; this is strongly supported by the observation that this bond lengthening of 0.06 Å in the Mephos complex, an Ni^{II} complex with a presumed configuration of $d_{xy}^2, d_{xz}^2, d_{yz}^2, d_{z^2}^2$, is approximately twice as great as that of 0.03 Å observed in the dimethylphenylphosphine complex, a complex with a presumed configuration of $d_{xy}^2, d_{xz}^2, d_{yz}^2, d_{z^2}^1$. The observed axial–axial bond angle of 176° and 179° respectively in these two complexes is substantially greater than that of 170° for the calculated model (Fig. 5(b)) and might be explained in terms of some π-bonding between the metal atom and the axial ligands.

Three complexes, Nos. 40, 42 and 43 in Table 1, possess a geometry similar to that of the calculated model in Fig. 5(c). This geometry, often called triangular bipyramidal, is found when some factor has prevented the formation of a regular trigonal bipyramidal geometry. The distortion in the complex $[Ni(Etphos)_3(CN)_2]$, XIII (No. 42), is due, at least in part, to the asymmetrical nature of the phosphine ligands; that in the complex ion $[Cu(bipyridine)_2I]^+$, XXXII (No. 43), with angles in the trigonal plane of 124°, 114° 122°, is mainly due to the larger size and greater repulsive power of the iodine ligand; that observed in the complex $[Co^I(CNMe)_5]^+$ ion, XXVII (No. 40), seems to be due to some electronic factor, probably a Jahn–Teller effect.

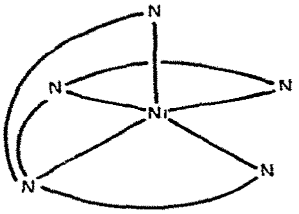
In each of these cases the slight increase in interligand repulsion is more than off-set by the energy gain achieved when a distortion from the regular trigonal bipyramidal geometry can occur.



XXXI



XXXII



XXXIII

Structures: XXXI, $[Ni(PPhMe_2)_2Br_3]$; Ni – P = 2.26 – 2.27 Å. XXXII, $[Cu(bipyridine)_2I]^+$. XXXIII, $[Ni(tepen)]^{2+}$.

E. CONCLUDING REMARKS

It follows from the preceding sections that when the geometry of a five-coordinate complex is under investigation due consideration must be given to the possibility of its possessing a geometry intermediate between the trigonal bipyramidal and square pyramidal forms. This is especially true when spectroscopic data appear to be in conflict. It is appropriate here to consider $[M(tepen)]^{2+}$ complexes, where tepen is *N,N,N'*-tris[2-(2'-pyridyl)ethyl]-ethane-1,2-diamine. The high-spin complex, $[Ni(tepen)](ClO_4)_2.CH_3NO_2$, has been observed to have a distorted square pyramidal geometry XXXIII[80] about the nickel atom with apical-to-basal bond angles ranging from 95 to 102°. It is considered that an intermediate geometry is possible for $[M(tepen)]^{2+}$ complexes in which the CFSE does not favour a C_{4v} symmetry relative to a D_{3h} symmetry as much as it does for high-spin nickel complexes and in which the presence of metal ions smaller than Ni^{II} effects a larger intra-chelate repulsion. The copper (II) complex, which fits both these requirements, is interesting as its ESR spectrum suggests a square pyramidal geometry while its absorption spectrum suggests a trigonal bipyramidal geometry[81].

Dawson et al.[82] have reported an unusual feature in the electronic spectra of several five-coordinate complexes when the temperature is lowered from 295 to 100 K. These complexes, $[Ni(CN)_2(PhPR_2)_3]$ where R is Me or OEt and $[MXL]^+$ where M is Ni^{II}, Pd^{II}

or Pt^{II}, X is a unidentate anion and L is a quadridentate phosphine or arsine tripod, have spectra in which the lowest frequency band is usually asymmetric and may even be split into a double peak at room temperature. The tendency for this band, identified as the ${}^1A_1' \to {}^1E'$ transition $[(d_{xz}, d_{yz})^4(d_{xy}, d_{x^2-y^2})^4 \to (d_{xz}, d_{yz})^4(d_{xy}, d_{x^2-y^2})^3(d_{z^2})^1]$, to become more symmetrical at lower temperatures suggests that the geometries of these complexes distort from the trigonal bipyramidal form (with D_{3h} symmetry) and become more intermediate in type (with C_{3v}, C_{2v} or C_s symmetry) as the temperature is increased.

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