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THE STERIC EFFECT IN BIS(2,2'-BIPYRIDYL) AND BIS(1,10-PHENANTHROLINE) METAL COMPOUNDS

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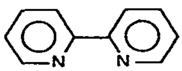
ABBREVIATIONS

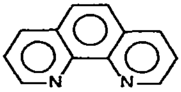
bipy	2,2'-bipyridyl
phen	1,10-phenanthroline
trien	triethylenetetraamine
impy	2-imidazolyl-2-pyridyl

A. THE PROBLEM

This is concerned with the steric effect in bis-chelated metal compounds of the ligands 2,2′-bipyridyl (I) and 1,10-phenanthroline (II).



I



II

The dimensions of these chelates are such that the planar (*trans*) disposition of two of them about a metal atom, with normal metal–nitrogen bond distances, results in an impossibly close approach of the α-hydrogen atoms of opposite ligands. Fig. 1 shows the situation for a metal–nitrogen distance of 2 Å. The "normal" Van der Waal's radii of the α-hydrogens are represented by the circles. In this idealised case, the non-bonded hydrogen atoms have an internuclear separation of only ~ 1 Å. Obviously the configuration must distort in some manner so as to relieve this steric strain.

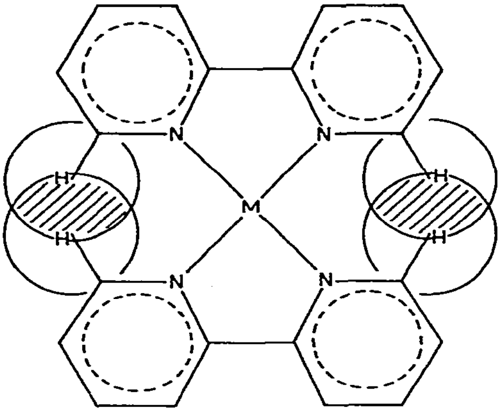


Fig. 1. The "steric effect" in a *trans*-bis(bipyridyl) metal compound. This represents the situation in an undistorted molecule with M–N distance of 2.0 Å. The circles give the "normal" Van der Waals radii of the H atoms (1.2 Å).

One obvious "distortion" would be to a *cis* rather than a *trans* configuration of an octahedral metal compound or ion $[M(chelate)_2X_2]^{n+}$.

The first reference in the literature to this steric effect appears to be a statement by James and Williams[1]. Soon after, it was noted in print by a number of Australian authors[2–5]*. These and more recent references[6–12]*, with the possible exception of Ref. 5, all have a common origin in a comment by B. Bosnich during the discussion of a paper presented by the author to an ANZAAS conference in Brisbane in 1961, and subsequent calculations of the interatomic distances by Barclay and Hoskins[13].

There has been more general, but still incomplete, recognition of this steric effect in the recent literature (see Section F); and it is becoming a reasonably common practice

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* Refs. 4,8 and 9 quote the author's Ph.D. thesis (1962); the patronymic is misspelt.

to assign the *cis* geometry to octahedral species simply on the basis of it. This development is not entirely to be encouraged, but it at least shows an awareness of the problem. Rund[14] and Palade[15] have recently discussed the geometric incompatibility of such a planar [M(chelate)$_2$] species in terms different from the above.

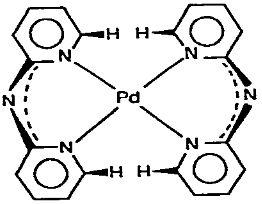
B. STERIC EFFECTS–SOME GENERAL POINTS

Recognition of this steric effect has been slow, in parallel with the general recognition of the detailed effects of the non-bonded ligand atom interactions in metal complexes. Probably part of the reason for this was the low standing of "steric effects" amongst many coordination chemists in the late fifties and early sixties. This resulted, at least partially, from the over-enthusiastic use of them, for example, to rationalise the non-existence of compounds or isomers. As more and more sterically "impossible" or "improbable" compounds were characterised it was observed that metal complexes often have a variety of means of alleviating steric strain, and "steric effects" tended to fall into some disrepute. Recent years fortunately have seen a more rational approach to the problem.

Steric effects are not an "all-or-nothing" affair. It may be possible to state that there is a finite (repulsive) force which has to be overcome in some specified arrangement of the bonding atoms. But, provided the bonding energy exceeds the loss from the steric interactions, the compound can exist.

Conversely, the existence of a compound, which is predicted to be unstable in some way, is not an argument for the non-existence of the steric effects.

As has been noted in a discussion of the steric effect in aromatic hydrocarbons, small deviations from the ideal geometry of a number of bond angles in a polyatomic compound can alleviate an apparently major steric effect at little cost in energy[16]. An example from transition-metal chemistry is the compound III, in which the ligands twist in such a way that the α-hydrogen atoms of opposite ligands are above and below the PdN$_4$ plane[17].



III

Steric effects may be manifested simply as tendencies for or against the formation of a molecule or a particular conformation of a molecule; and the obviousness of the manifestation will, of course, depend on the size of the steric effect. Repulsion terms of the order of several kcal·mole^{-1} may be completely swamped by other, essentially non-bonding forces such as different solvation energies of alternative conformations in solution, or the total lattice forces of the various solid forms in which the compound may crystallise. This is particularly true for metal compounds, which we can seldom, if ever, study in the gaseous state or in solution in non-polar solvents.

The significance of the steric effect also will depend on the differences in bonding energy of alternative structures. For example, in an octahedral species $[M(chelate)_2X_2]^{n+}$, *cis* and *trans* isomers probably have much the same total bonding energies; and the complete absence of one isomer may result from small differences in non-bonded interactions (this may not be true if π-bonding energies are significant—they could favour the *cis* configuration).

However, in the case of palladium(II) and platinum(II), for example, we know from chemical experience that the planar MN_4 geometry is distinctly favoured over any other geometry (five-coordinate, or six-coordinate). In this case, if the bis(chelate) compounds are to form at all, gross distortions of the chelate itself may be as likely as any distortion or rearrangement of the coordination polyhedron.

C. CALCULATIONS OF THE VAN DER WAALS REPULSION ENERGY

In order to indicate the possible magnitude of the steric effect, some simple calculations have been carried out[18]. We have considered only the non-bonded interactions of the opposing α-hydrogen atoms in *rigid* chelates, and have allowed the ligands to twist with respect to the undistorted coordination polyhedron as indicated in projection in Fig. 2. This rigid chelate model is not justified in calculations with any pretension to reality. However, we note that the distortion of these ligands will require distinctly more energy than, for example, that of the ligands in compound III; and the size of the effect which the simple calculations show indicates that it will not be alleviated by small ligand distortions. There are not enough bonds here over which to spread the angular distortions required in sufficiently small increments. In view of the impossibility of making exact calculations on these systems, and until suitable structural data become available, these calculations are as good a starting point as any.

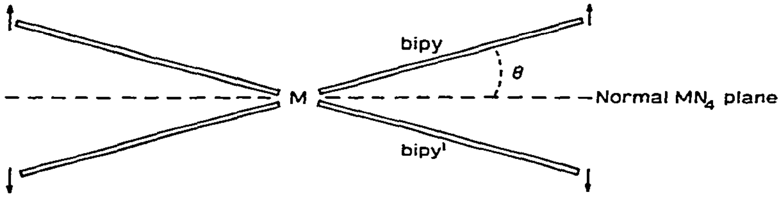


Fig. 2. The direction of mutual twist of the ligands, with respect to the normal MN_4 plane, for which the calculations have been made.

The geometry of bipyridyl (Fig. 3) used in the calculations was derived from published bond lengths and angles in known crystal structures of bipyridyl compounds (references are listed in Table 1), and the more accurate values for pyridine[19] and biphenyl[20].

Various metal–nitrogen distances were considered, and the total Van der Waals energy was calculated at 1° increments of the angle of twist of each bipyridyl (θ in Fig. 2).

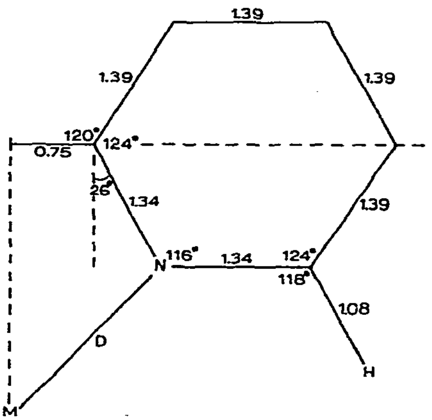


Fig. 3. The geometry of bipyridyl and the coordination polyhedron used in the calculations.

TABLE 1

THE DIHEDRAL ANGLE BETWEEN THE PYRIDYL RESIDUES IN SOME KNOWN BIPYRIDYL STRUCTURES

Compound	Dihedral angle	Ref.
Bipyridyl	Planar	29
$[Cr(bipy)_2(O_2)_2O]$	Planar[a]	30
$[Cu(bipy)_2I]I$	2° and 10°[b]	2
$[Cu(bipy)_2NO_2]NO_3$	10.8° and 11.6°	31
$Cu(bipy)(NO_2)_2$	3.2°	32
$[Ga(bipy)_2Cl_2]\,[GaCl_4]$		33
$[Mo(bipy)Br_2O_2]$	3.1°	34
$[Mo(bipy)(CO)_3Cl(SnMeCl_2)]$	4.7°	35
$[Ir(bipy)(CO)I_2(C_2H_3O_2)]$	7.5°	36
$Pt(bipy)(acac)(Me)_3$	Planar	37

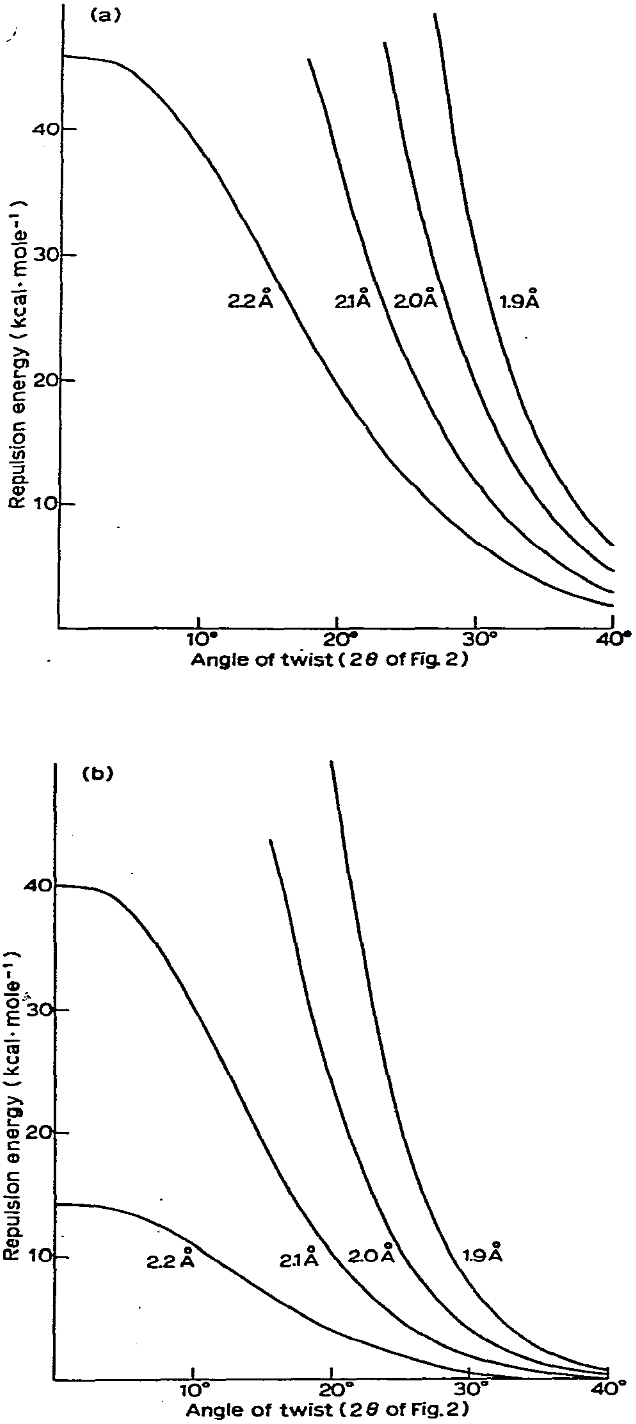
[a] Two crystalline forms were studied. The chelate lies on a crystallographic mirror plane in one of them, and is planar, within experimental error, in the other. [b] The angles may not be significant.

The calculations used a variety of different sets of parameters for the equation[16].

$$U = -AR^{-6} + B\exp(-CR)$$

The results from three sets of such parameters, which have been used by other workers, are given in Figs. 4(a), (b) and (c), and each gives the results for four different metal–nitrogen bond lengths (D in Fig. 3). The parameters of Mason and Kreevoy[21] give a "hard" model (Fig. 4(a)); those of Hill[22] give a "soft" model (Fig. 4(c)); while those of Bartell[23] give an "intermediate" one (Fig. 4(b)). The variety of such curves could be multiplied using the variety of parameters applied to aromatic hydrocarbons. The curves give the total Van der Waals energy (repulsive) for the pair of bipyridyl molecules, plotted against the dihedral angle between their projected planes (i.e. 2θ in Fig. 2).

On the basis of these figures, it is evident that there is still a very significant steric effect in the *trans*-configuration for a rather long metal–nitrogen distance of 2.2 Å. Its


(a)
Repulsion energy (kcal·mole⁻¹)
40
30
20
10
2.2 Å
2.1 Å
2.0 Å
1.9 Å
10°
20°
30°
40°
Angle of twist (2θ of Fig. 2)
(b)
Repulsion energy (kcal·mole⁻¹)
40
30
20
10
2.2 Å
2.1 Å
2.0 Å
1.9 Å
10°
20°
30°
40°
Angle of twist (2θ of Fig. 2)

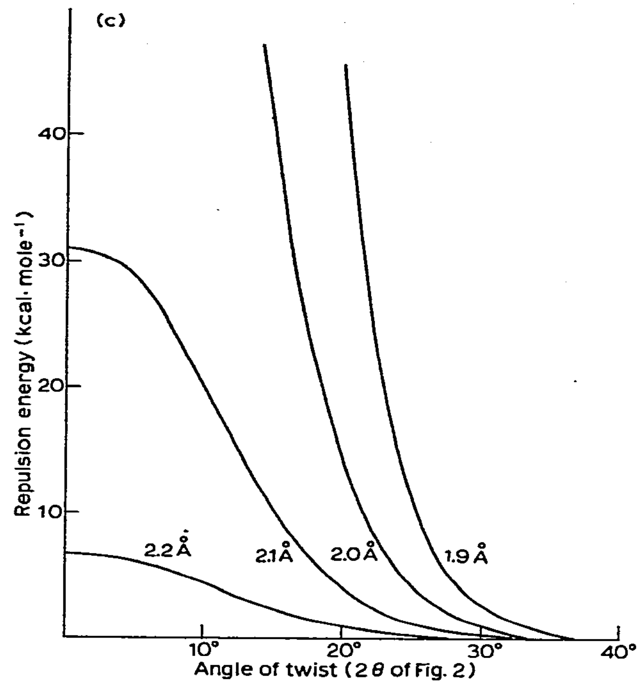


Fig. 4. The repulsion energy vs. angle of twist of the ligands using: (a) the parameters of Mason and Kreevoy[21]; (b) those of Bartell[23]; and (c) those of Hill[22].

size will depend upon which of the sets of parameters chosen corresponds closest to the reality. Most metal-nitrogen distances, with which we will be concerned, fall well within this distance, and a great many are at ~ 2.0 Å, where quite large angles of twist are required to relieve the steric effect. Even in the case of the softest model (Fig. 4(c)) a twist of 30° is required to reduce the repulsion below 1 kcal·mole^{-1}; and, if the harder model is applicable, this angle increases to about 50°.

Such gross distortions of the coordination polyhedron are undoubtedly energetically unfavourable for most metals. It should not be concluded that non-bonded hydrogen-hydrogen distances less than the sum of their Van der Waals radii will not exist. Many "overcrowded" aromatic hydrocarbons are known in which these are as low as 1.8 Å (this corresponds to a dihedral angle, 2θ, of 30° for a metal-nitrogen distance of 2.0 Å, in our system.) However, these short contacts do not imply a lack of strain in the molecules. The planar structure of biphenyl in the solid state[24] has sometimes been taken as an indication that the Van der Waals repulsion energy between hydrogen atoms has been overestimated. Two close H-H contacts of between 1.9 and 2.0 Å are observed (this depends on the C-H distance which is not accurately known). However, the *p*-bitolyl molecule packs in the crystal with angles of about 40° between the two *p*-tolyl moieties[25], and biphenyl has a similar twisted structure in the gaseous state. Both correspond to calculated energy minima[25]. The planar arrangement of biphenyl in the solid appears to result from intermolecular forces which swamp the intramolecular repulsions.

Solid biphenyl is an indication[16] (and there are many others[16]) that the softer model for the calculations is preferable for the hydrocarbons. It does not necessarily follow that this is so in our systems.

Our calculations neglect:

(*a*) charge redistribution which occurs on bonding to the metal;

(*b*) interaction of the H atoms with metal orbitals, which may be significant and almost certainly dependent on angle. ^{1}H NMR results of phenanthroline compounds have been interpreted as evidence for such interaction[26], and preliminary results with complexes of tetramine ligands containing pyridyl residues[27] may indicate similar complications. A spherically symmetric correction for the metal as used by Gollogly and Hawkins[28] may only compound the errors;

(*c*) other non-bonded interactions. These include other atom–atom interactions within the complex, and the interactions with other molecules. The molecules will always be in contact directly with their "environment". It is seldom possible to study metal compounds in the gaseous state or even in solution in non-polar solvents. Specific solvation effects and solid-state effects (the interaction energies in various crystalline lattices) may be just as important in some cases in defining configuration as the intramolecular interactions.

This is certainly true in the case of metal compounds of the facultative quadridentate ligands triethylenetetramine (trien), and its homologues[6]. Intramolecular steric effects favour either a *cis*- or a *trans*-octahedral configuration of the compounds $[MN_4X_2]^{n+}$ for the different ligands[6]; but whether *cis* or *trans* isomers of $[Ni(tetramine)(solvent)_2]^{2+}$ are formed in solution depends more on the specific solvation energies than the intramolecular non-bonded interactions[38];

(*d*) entropy terms;

(*e*) metal-ligand bonding energies. For example, π-bonding between the metal and the chelates in octahedral structures may favour a *cis* over a *trans* configuration;

(*f*) other modes of distortion of the coordination polyhedron and/or the ligands.

The ligands may twist with respect to the coordination polyhedron in much the same way as do the ligands in the palladium compound III[17]. The angular distortions required are very similar to those in the case calculated.

Bipyridyl has a degree of freedom not available to phenanthroline. It can twist about the C(2)—C(2′) axis; and such a twist, in conjunction with either of the distortions of the polyhedron, will help to relieve the overcrowding. Such a twist is indeed observed in many of the known crystal structures of bipyridyl compounds (Table 1). It probably results, at least in part, from another atom overcrowding which occurs in the ligand itself. The 3 and 3′ hydrogen atoms are well within their normal Van der Waals radii, as in the case of biphenyl noted above.

Rund[14] gives a preliminary report of an X-ray structural study of $[Pd(phen)_2](ClO_4)_2$ which indicates that the ligands are "bowed" about their C_2 axis. We look forward to the full structural report.

Whether, and how, these distortions are to be considered in the calculations must depend upon a knowledge of the energy curves for the distortion of the metal–ligand bond lengths and angles. Provided (*a*) above is insignificant, reasonable calculations of the distortion of the ligands could be made. However, there seems to be little point in doing this in the absence of any knowledge of how the coordination polyhedron may distort. The situation will change when detailed structural data becomes available on structures in which such distortions occur; but in the meantime we think the above calculations as useful as any in giving a rough guide to the expected steric effect. It may be greater than the calculations imply–it may be less. There is no way yet of deciding.

D. EXPECTED CONSEQUENCES OF THE STERIC EFFECT

The effects will be different in the various coordination polyhedra, so some general comments are pertinent before the individual metals are discussed.

(i) *Octahedral compounds*

In all systems governed simply by equilibrium thermodynamics–systems in which equilibria are rapidly attained–the *cis*-octahedral configuration should occur to the almost complete exclusion of the *trans* configuration. It is unlikely, in view of the apparent magnitude of the effect, that different solvation energies or crystal packing effects will be sufficient to stabilise the *trans* configuration, except at rather long M–N distances. The compounds of the first-row transition metals in oxidation state 2+ belong to this class of "labile" compounds.

On the other hand, the chemistry of the compounds of transition metals in oxidation state 3+, such as Cr^{III}, Co^{III}, Rh^{III} and Ir^{III}, often is controlled by reaction energetics. Compounds with "unstable" structures exist because they undergo reaction in the medium at a slower rate than that of the reaction which produces them. It is therefore often possible to isolate and study the less stable isomers. For example, different conformation energies and cumulative ring strain define[6] the *trans* isomer of the complex $[Co(trien)Cl_2]^+$ as unstable with respect to the two *cis* isomers. However, under carefully chosen conditions, it is possible to isolate[39] *trans*-$[Co(trien)Cl_2]Cl$ and $[Co(trien)Cl_2]ClO_4$. At equilibrium, only *cis* isomers of $[Co(trien)X_2]^{n+}$ species exist in solution[6]. The fact that either *cis*-α or *cis*-β isomers exist at equilibrium for different X, has been taken as evidence that there is no steric strain in trien complexes[39]. However, the existence of an unstable isomer is not evidence for the non-existence of a steric effect. This is another case in which different solvation energies swamp the steric effect.

Hence, the most likely compounds to give a *trans* configuration of $[M(bipy)_2X_2]$ or $[M(phen)_2X_2]$ are those of metals with large covalent radii, which are kinetically stabilised.

Another possible source of a (grossly distorted) *trans*-octahedral configuration may be the compounds of metals which normally have distorted polyhedra. For example, a not uncommon geometry in the known crystal structures of copper(II) compounds[40] is that shown in Fig. 5. It can be regarded as being formed from a *trans*-$[CuA_4B_2]$ octahedron by imposing a tetrahedral distortion on the CuA_4 unit (and the Cu–B bonds usually are elongated). For two phenanthrolines (or bipyridyls) occupying the A sites, such a distortion would alleviate some of the H—H non-bonded interaction. This is an example pertaining to the statement in Section C that the distortion vs. energy curve will be different for the coordination polyhedra of different metals.

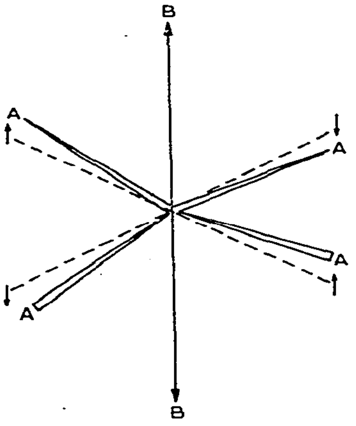


Fig. 5. One of the known coordination polyhedra of copper(II) compounds.

(*ii*) *Square coplanar compounds*

This geometry is well characterised, for example, in Ni^{II}, Pd^{II}, Pt^{II}, and to some extent in Cu^{II} compounds. Contrary to a still widespread belief, perhaps emanating from valence bond theory, this geometry is very much rarer for Cu^{II} than for Ni^{II}.

There are two extreme cases here: (*a*) metals for which other coordination polyhedra are accessible, such as Ni^{II} and Cu^{II}; and (*b*) metals such as Pd^{II} and Pt^{II}, for which distortions of the planar geometry and changes to other coordination polyhedra cost too much in energy. Some recent crystal structures[41] of distinctly overcrowded bis[salicylaldiminatopalladium(II)] compounds show clearly that this metal distinctly "prefers" a square coplanar geometry.

In the case of metals like Cu^{II} and Ni^{II}, the other coordination polyhedra, cf. (iii) below, are expected to occur with the complete exclusion of the planar geometry. However, for Pd^{II} and Pt^{II} we may expect the coordination polyhedron to distort as little as possible, at the expense of distortions in the ligands themselves, if the species are to exist at all; and they should be distinctly unstable. But this is partly a rationalisation of known facts (see Section F).

(*iii*) *Other coordination polyhedra*

In structures such as tetrahedral $[M(\text{chelate})_2]X_n$, and five coordinate, essentially trigonal bipyramidal $[M(\text{chelate})_2X]^{n+}$ (cf. Ref. 2) the α-hydrogen atoms are not opposed.

These, and now the *cis*-octahedral geometry[31], are the geometries found for the Cu^{II} compounds (q.v.), probably at least partially because of the steric effect. The five coordinate geometry may occur in other first-row transition-metal compounds, but although we have looked for them[7,27] we have found none yet.

Higher coordination numbers, as in $La(bipy)_2(NO_3)_3$[42], have a variety of possible structures, and usually long M–N bonds (e.g. 2.6–2.7 Å in the La^{III} structure). The problem of the steric effect, for two ligands in opposed symmetrical planar array, generally will not be pertinent.

E. METHODS USED TO ASSIGN CONFIGURATION

The isolation of two compounds of empirical formula $M(chelate)_2X_n$ is not *of itself* evidence for *cis* and *trans* isomers. Some authors appear to assume this[43]. Besides the problem of polymorphism of the same compound[10,11,12], other forms of isomerism are possible, such as $[M(chelate)_2X_2]$ and $[M(chelate)_3]\,[M(chelate)X_4]$.

A recent note[44] assigns the configuration of some chromium(III) and cobalt(III) compounds partially on the basis of "chemical correlations". Rather, other physico-chemical evidence for configuration should be used to check if any stereo-change has occurred during these reactions. Such "methods" are a carry-over from the classical proofs of structure in carbon chemistry, and their usefulness in the chemistry of metal compounds is yet to be established. It is unlikely to be very great.

(*i*) *Diffraction methods for solids*

X-ray (and neutron) diffraction methods are almost the only ones that give unequivocal answers about structure in the solid state. Although other methods, as noted below, may be useful in special cases, the recent tendency to refer to the former as "non-sporting" and the latter as "sporting" methods is mistaken. One seldom has even a "sporting" chance of success with the latter, and the results usually are interpreted in terms of a specific prejudice rather than on the basis of any real evidence.

X-ray methods are rather expensive in time, or more recently in equipment; and very few structural analyses yet are available on the compounds of interest here.

For the series of kinetically stabilised compounds $[M(phen)_2Cl_2]X{\cdot}nH_2O$, there is a key structure available[45]—that of *cis*-$[Co(phen)_2Cl_2]Cl{\cdot}3H_2O$, Unfortunately, the published refinement of this structure is incomplete, with the R value standing at 21% for 1000 reflections. Even at this level of refinement the basic geometry of the cation is unlikely to be incorrect, but the e.s.d's for the atom positions will be very high. There is probably no difference in the published Co–N bond lengths of 1.96, 1.98, 2.03 and 1.96. Further, the hydration number cannot be accepted as proven. Another molecule of water could well have been missed, unless specifically sought, and we suspect that the compound is a tetrahydrate. Many analyses on this particular crystalline species[18], and its isomorphous Cr^{III} [11] and Rh^{III} [12] analogues, indicate a tetrahydrate, as does the "X-ray molecular weight" of the chromium species[11].

From such key structures, proof of structure in analogous compounds with other metals can be obtained by the use of X-ray powder photography (Debye–Scherrer method). This technique could be used more profitably in coordination chemistry than many other more widely used physical methods. The answers which it gives cannot be as unequivocal as those from three-dimensional structural studies, but in many cases similar powder patterns of analogous compounds must, for all practical purposes, imply essentially the same geometry. This will be especially true in the present case where the question is usually one of gross differences in geometry, as between *cis*- and *trans*-octahedral isomers of large flat chelates.

With major changes in the atomic number of the atoms present, as in the compounds *cis*-$[Cr(phen)_2Cl_2]X \cdot 4H_2O$ (X = Cl, Br and I), distinct differences in the powder patterns are to be expected even if the compounds are isostructural. In such cases, the relationship between the structures may be difficult to discern from their powder patterns alone. It is then useful to have a few single crystal X-ray photographs to determine the space group and unit cell, as we have done in the case of the above chromium compounds[11]. The known unit cells and space groups for the compounds $[M(phen)_2Cl_2]X \cdot nH_2O$ are listed in Table 2.

TABLE 2

THE UNIT CELLS AND SPACE GROUPS OF CHROMIUM AND COBALT COMPOUNDS $[M(chelate)_2Cl_2]X \cdot nH_2O$

Compound	Space group	Unit cell			
		a	*b*	*c*	β
α-*cis*-$[Co(phen)_2Cl_2]Cl \cdot xH_2O$	C_c	15.46	13.50	12.28	90.2
α-*cis*-$[Cr(phen)_2Cl_2]Cl \cdot 4H_2O$	C_c or $C_{2/c}$	15.7	13.6	12.5	100.5
cis-$[Cr(phen)_2Cl_2]Br \cdot 4H_2O$	C_c or $C_{2/c}$	15.7	13.7	12.5	100
cis-$[Cr(phen)_2Cl_2]I \cdot 4H_2O$	C_c or $C_{2/c}$	15.5	13.7	12.9	101.2
δ-*cis*-$[Cr(phen)_2Cl_2]Cl \cdot 2H_2O$	P_{bcn}	12.8	12.3	16.4	
cis-$[Cr(bipy)_2Cl_2]I$	$P2_12_12$ or $P2_12_12_1$	17.0	11.1	11.7	
α-*cis*-$[Co(phen)_2Br_2]Br \cdot 3H_2O$	C_c or $C_{2/c}$	[a]			

[a] The unit cell data are not given in the abstract[69].

Using powder techniques, Rh^{III} [12,50] and Ir^{III} [50] cations $[M(chelate)_2X_2]^+$ also have been shown to be *cis*. In section F a variety of analogous compounds with different metals will be noticed, for which there is no reliable structural data. Comparison of their X-ray powder patterns with those of the above compounds would be the simplest method of determining structure, provided there are not too many complications from polymorphism.

This latter is the major problem encountered in the use of X-ray powder data and unit cell determinations in defining structure. For example, five different polymorphs (or perhaps different hydrates in one or two cases) of the compound *cis*-$[Cr(phen)_2Cl_2]Cl \cdot nH_2O$ were encountered[11], as well as solid-state changes from one crystalline form to another.

Such polymorphism is quite common in phenanthroline and bipyridyl metal compounds[11,12,18,27], and in almost every metal–chelate system we have studied in Sheffield in the last few years[10,11,12,18,27,46] it has complicated the work. (The record to date is eight crystalline forms of a compound Cu(tetramine)(NCS)$_2$ obtained from water and a ninth one from ethanol and ether[18]. Here also solid-state changes from one crystalline form to another have been observed.)

Similar powder patterns (line position and intensity) of analogous compounds are a good test of the same basic structure of the molecular species; but from different powder patterns we can deduce little of significance. The latter do not prove different molecular structures, but may simply refer to polymorphs of the same molecular species.

One other use of X-ray powder patterns may be noted[46]. They are an excellent fingerprint, and could profitably be as widely used for this purpose as melting points have been in carbon chemistry. We have found a number of examples where the occurrence of polymorphism makes it almost impossible to define the particular crystalline species prepared by previous workers.

(*ii*) *Electronic spectra*

As more structural data become available, it is becoming increasingly apparent that the use of electronic spectra for making structural assignments must be very much more restricted. However, for a few metals in some oxidation states, they still appear to give reliable results. In particular, the *d-d* spectra of the cations of the generic type $[CoN_4X_2]^+$ and $[CrN_4X_2]^+$ show marked and characteristic differences for *cis* and *trans* isomers, provided X is sufficiently far from N in the spectrochemical series. We can

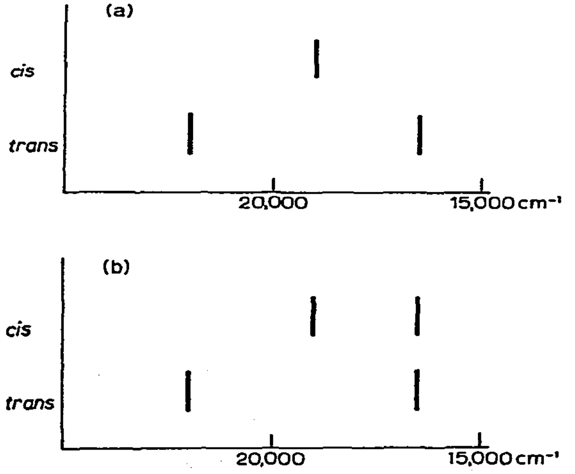


Fig. 6. Band patterns in the electronic spectra of *cis* and *trans* isomers of $[CoN_4Cl_2]^+$ and $[CrN_4Cl_2]^+$.

predict[11,47,48] with some degree of confidence that the *d-d* bands for the cations *cis*-$[M(chelate)_2Cl_2]^+$ (M = Co, Cr; and chelate = phen, bipy) should appear at ~ 16,500 and 19,000 cm^{-1}; while those for the *trans* isomer should occur at ~ 16,500 and 22,500 cm^{-1} (Fig. 6(b)). Other *d-d* bands at higher energy are of no concern since they will be lost in the more intense ligand π-π^* and charge-transfer absorptions. Similar remarks apply[49] to the spectra of Rh^{III} and Ir^{III} but in these cases the *d-d* bands all occur at too high an energy to be resolved from the other more intense absorptions[12,50].

In practice, the first band for the *cis* isomer of a cobalt(III) compound is often of such low intensity, that, as in *cis*-$[Co(en)_2Cl_2]^+$, it is not easily detected in the room temperature electronic absorption spectrum—i.e., the pattern observed is often that of Fig. 6(a) rather than 6(b).

The other transition metal for which the electronic absorption spectra can be used in this way is nickel(II). In this case[51] the absorption bands of interest are well out in the near IR region between ~ 8000 and 18,000 cm^{-1}, and are not obscured by other electronic absorption processes. The theory is essentially the same as for Cr^{III} or Co^{III}, and in practice the observed "splitting" pattern is that of Fig. 6(a). All of the spectra of the compounds $Ni(chelate)_2X_2$ which we have recently measured are consistent with a *cis*-octahedral structure[27].

(*iii*) *Vibrational spectra*

These sometimes can be of use, but there is widespread misuse of such methods Two independent methods, which have been used to assign structure to the compounds of interest here, now have been shown[11] to be untenable in practice.

The first[52], and least firmly based, relied on the number of CH bending vibrations in the 700–800 cm^{-1} region. Of the ten compounds originally chosen to illustrate the "method", one already failed to fit the predicted pattern, and the assumed *trans* structure of three more of the ten now is known to be wrong[11]. The nickel(II) compounds are *cis*[7,27], and the compound accepted as *trans*-$[Co(bipy)_2Cl_2]Cl$ is a complex mixture[10] containing *cis*-$[Co(bipy)_2Cl_2]^+$ and $[Co(bipy)_3]^{3+}$ cations. Thus, from the original table, it is possible to say only that *cis*-bis(bipyridyl) species may have two, three, or four discrete bands in this region of the vibrational spectrum. We find even more variety in this region for different salts (and their polymorphs) of the cation *cis*-$[Cr(bipy)_2Cl_2]^+$, which shows clearly the wide variation of vibrational spectra that the same molecular species can exhibit in different crystalline environments[11].

This cation previously had been assigned[53] a *trans* configuration in the compound $[Cr(bipy)_2Cl_2]Cl \cdot 2H_2O$ on the above IR criterion. But even if the method had any basis in theory or practice, Baker and Phillips[53] were in error in recording only two bands. We find five for the same species[11]. (Their assignments of the electronic spectra also were in error.)

Other vibrational methods rely on the MX_2 skeletal vibrations. For the *trans* geometry (i.e. for linear X-M-X) only one IR active vibration should be observed, whereas two are expected for the bent MX_2 unit in the *cis* isomer. This method has been applied to the metal–halogen stretching frequencies of the Rh^{III} and Ir^{III} compounds; and two groups[50,54] have "proved" the *cis* configuration with different assignments of the metal–halide stretching vibrations. There are obviously some pitfalls in the use of the method.

Methods using vibrational spectra are limited by the following:

(*a*) They rely on a group frequency concept, which may not hold, even approximately, in the compounds of interest.

(*b*) The coupling between the various M–X vibrations (or X vibrations in the case of, e.g., NCS, CN, etc.) may be quite small, and therefore unobservable. Because of this, the observation of two bands may be evidence for the *cis* isomer, but only one band is not necessarily evidence for the *trans* isomer. (The usual problem of negative evidence.) Related to this is the problem of the resolving power of the instrument.

(*c*) "Solid-state effects" may complicate the problem. Many compounds are studied in the solid state, and unfortunately we do not know enough about solid-state effects, which may cause band splitting just as well as molecular symmetry effects (see, e.g. Ref. 55). In addition, hydrogen-bonding and other direct interatomic interactions may add further complications.

It is therefore preferable to measure the vibrational spectra in solution, if possible; but there may be problems of rearrangement in solution if the species are labile. In this case, the solid state and solution measurements may refer to different species.

One saving grace, in the case of the phenanthroline and bipyridyl compounds, is that the large ligands appear effectively to dilute the MX_2 units. Thus, following our earlier study[5,27,56] of the isothiocyanato compounds $[M(chelate)_2(NCS)_2]$ (cf. also Ref. 57), we have recently looked for solid-state effects in the IR spectra of a number of these compounds in the C≡N stretching region. There appear to be no such complications[58], and the assigned *cis* configuration for such species with two bands near 2100 cm^{-1}, separated by ~ 10 cm^{-1}, has recently been confirmed by an X-ray structural determination[59] of one polymorph of $[Fe(bipy)_2(NCS)_2]$.

(*d*) Even if the above complications do not apply, there may be severe practical difficulties in assigning the origin of the observed vibrations. The occurrence of other bands[11] in the same region as that of the M–X stretching modes of the cations $[M(chelate)_2X_2]^+$ (X = Cl, Br) is obviously the reason for the two different assignments[50,54] of the Rh–Cl and Rh–Br stretching modes. This appears to be the main reason why assignments of molecular symmetry from metal–halogen stretching frequencies are unreliable. The same is apparently not true for $M\text{–}(X\text{–}Y)_2$ vibrations, where the X–Y vibrations come in a major "window" area at 2000 cm^{-1} (i.e. CN, NCS, CO, etc.).

The most satisfactory use of vibrational methods in the compounds of interest here is in the proof of *cis* structure[60] for the cation $[Fe(phen)_2(CNH)_2]^{2+}$ in liquid HF. Similarly, the two bands in the IR spectrum near 2100 cm^{-1} for the compound $[Co(bipy)_2(NCS)_2]$ in acetone prove the *cis* structure in this solvent[27].

(iv) *Magnetic resonance methods*

^{1}H NMR methods recently have been applied to the problem of structure of these bis(chelate) species. Good structural assignments are available for $[Fe(phen)_2(CNH)_2]^{2+}$ in liquid HF[60] and $[Ir(bipy)_2Cl_2]^{+}$[64]. An example of misuse of the method is given by the suggestion[61] that the ^{1}H NMR spectrum of a green compound, supposed to be *trans*-$[Co(phen)_2Cl_2]Cl$, was evidence of the *trans* structure. The green compound was not properly characterised first, and, as we suggested[10], contains the $[CoCl_4]^{2-}$ anion. Josephsen and Schäffer[62] now have shown it to be *cis*-$[Co(phen)_2Cl_2]_2[CoCl_4]\cdot 2H_2O$, which is probably the same crystalline species that we reported[10] as $1.5H_2O$ (had the authors[62] reported the powder pattern which they measured, the doubt would have been resolved—cf. (i) above). Even less understanding of the ^{1}H NMR method is shown in a recent note[63].

Methods using ESR, on the other hand, cannot be expected to be of any significant use for a priori assignments of configuration, although they may be useful in *detecting* isomers. Gibson and coworkers[65] have considered their possible use for Mn^{II} compounds, but note that significant differences between *cis*- and *trans*-octahedral isomers cannot be expected. An example of the detection of two isomers (?) is given by a recent study[66] of $[Cu(bipy)_2(H_2O)_x]^{2+}$ in a water–ethanol glass at low temperature. The two different resonances observed were interpreted as giving evidence for *cis*- and *trans*-octahedral diaquo isomers. Other interpretations are possible, and the variety of different structures, which also could explain the two resonances, are discussed in Section F.

(v) *The Mössbauer effect*

Here again is a method that can probably detect different species, but is unlikely to be of use for a priori assignment of structure. The method is at present limited to a few metals, the most conspicuous of which is iron. Schilt[67] quoted a report that different Mössbauer spectra had been obtained for $[Fe(phen)_2(CN)_2]$ isolated under different conditions, and used this as evidence for *cis* and *trans* isomers. However, later workers[68] have been unable to repeat these results, and it is possible that in the earlier work an oxidised material was obtained as one of the products.

F. A SURVEY OF KNOWN COMPOUNDS

Table 3 has been constructed in order to help in assessing the possible steric effect in the compounds of the different metals. It indicates the known or expected M–N (chelate) distances. Ionic radii also are listed to provide a comparison between known and unknown M–N distances. They should give a fairly reliable relative scale.

It is important to note that the steric effect decreases exponentially as the M–N distance increases, but there is no way yet of deciding at what distance it becomes insignificantly small.

TABLE 3

METAL-NITROGEN DISTANCES[a] FOR VARIOUS KNOWN OXIDATION STATES

	M-N (Å)	Compound	Ionic radii (M^{n+})[80]
Sc^{III}	[b]		0.686
Ti^{III}	[b]		0.61
V^{III}	[b]		0.625
V^{IV} (VO^{2+})	2.05	[VO(BAE)][70] (5-coord)	
Cr^{III}	2.05-2.10		0.608
Mn^{II}	2.2	$Mn(NH_2\text{-}NH\text{-}COO)_2\cdot 2H_2O$[71]	0.82
Fe^{II} high spin	2.17	*cis*-$[Fe(bipy)_2(NCS)_2]$[59]	0.77
low spin	2.03	*cis*-$[Fe(bipy)_2(NCS)_2]$[59]	
Fe^{III}	2.1	$[\{Fe(salen)\}_2O]\cdot(py)_2$ (5-coord)[72]	0.628
Co^{II}	2.1		0.72
Co^{III}	1.95-2.00		0.56
Ni^{II}	2.0-2.1		0.68
Cu^{II}	2.0-2.1	$[Cu(bipy)_2NO_2]NO_3$[31]	
Zn^{II}	2.05-2.1	$Zn(phen)Cl_2$ (tetrahedral)[73]	
Ga^{III}	2.10	$[Ga(bipy)_2Cl_2]\,[GaCl_4]$[33]	0.613
In^{III}	[c]		0.714
Tl^{III}	[c]		
Tl^{III}	[c]		
Mo(O)	2.31-2.35	$[Mo(dien)(CO)_3]$[74]	
Mo "oxidised"	2.23-2.45	(see Table1)	
W(O)	[d]		
Ru^{II}	2.1	$[Ru(NH_3)_5N_2]^{2+}$[75]	
Ru^{III}	[d]		
Os^{II}	[d]		
Os^{III}	[d]		
Rh^{III}	2.09	$[Rh(py)_4Cl_2]H(NO_3)_2$[76]	
Ir^{III}	2.13-2.15	(see Table 1)	
Pd^{II}	2.02	$[Pd(bipyam\text{-}H)_2]$[17]	
Pt^{II}	2.01-2.05	*cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$[77]	
Ag^{I}	2.15	[Ag(8-OH-quin)(8-*O*-quin)] py[78]	
Ag^{II}	2.1(?)		

[a] These refer to octahedral species, except where different geometries are specifically noted. Where three-dimensional structural data are known for a phenanthroline or bipyridyl compound, these only are included. Otherwise, other M-N distances have been quoted without reference to the variety of structures, but where only one such was accessible, or particularly pertinent, the compound to which it refers is listed. [b] No known M-N distances in octahedral species, but the "ionic radii" give an acceptable comparison with known bond lengths. [c] No known M-N distances, but in $[MCl_5(H_2O)]^-$ the $M\text{-}OH_2$ bond lengths[79] are: In, 2.23 Å; Tl, 2.19 Å. M-N distances should be ~ 0.1 Å less than these. [d] Again no known M-N distances, but they should be much the same as for the metals in the same or adjacent subgroups, i.e. ~ 2.3-2.4 for W, and ~ 2.1 for the Group VIII metals.

Before dealing with the compounds of each metal separately, the data on several series of compounds $M(chelate)_2X_2$, for the first-row transition metals, is noted. The structures of some of these have been related[81] by their X-ray powder patterns to the nickel(II) compounds (q.v.) whose structures are more readily definable[7,27]. This data is listed in Table 4. Those compounds which are isomorphous with a nickel(II) compound

TABLE 4

CORRELATIONS OF THE STRUCTURES OF THE COMPOUNDS M(chelate)$_2$X$_2$ FROM THEIR X-RAY POWDER DIFFRACTION PATTERNS[81]

Series	Metals giving isomorphous compounds[a]	Not isomorphous[b]
$M(phen)_2(NCS)_2$	Mn,Fe,Co,Ni,Cu	Zn
$M(phen)_2I_2$	Mn,Fe,Co,Ni	Cu[c]
$M(phen)_2(NO_3)_2 \cdot xH_2O$	Co,Ni(2H$_2$O)	Cu(1H$_2$O)
$M(bipy)_2(NCS)_2$	None, as yet	Fe[d], Co, Ni[e], Cu
$M(bipy)_2Cl_2$	None, as yet	Co,Ni[f]

[a] The nickel(II) compounds (q.v.) can be shown to be *cis*-octahedral, so the compounds of all metals in this column have this structure. [b] None of the compounds of the metals in this column are isomorphous with any other of the series. [c] Two different crystalline forms of the five-coordinate species [Cu(phen)$_2$I]I are characterised[27]. [d] Three polymorphs are described by König[82], but unfortunately he did not measure the X-ray powder patterns. Baker and Bobonich[83] give the *d*-spacings for one polymorph. [e] The compound [Ni(bipy)$_2$(NCS)$_2$] usually crystallises as solvates, and on loss of the solvent, it changes in the solid state to a brown crystalline material which appears to be [Ni(bipy)$_2$(NCS)]$_2$(SCN)$_2$. [f] This is based on a statement by Lee et al.[84] about the compounds prepared by thermal decomposition from the tris species. They did not publish the *d*-spacings.

can be confidently assigned a *cis* octahedral structure, but where the compounds are not isomorphous it does not follow that they are not *cis*; although we do know that a five coordinate geometry occurs in the copper(II) compounds (q.v.).

(*i*) *Scandium*

Two solid compounds of empirical formula $Sc(phen)_2X_3$(X = Cl, SCN) recently have been described[43]. They were assigned as *cis* and *trans* isomers of $[Sc(phen)_2X_2]X$, but with no significant evidence. Species such as $[Sc(phen)_3]$ $[Sc(phen)X_4]X_2$ have not been eliminated, and appear to be of more likely occurrence than the *trans* isomer here. (The assignments relied on untenable IR "methods"). Proper assignment of structure to these compounds must await X-ray studies—either comparative powder work or full three-dimensional structures.

(*ii*) *Titanium and vanadium*

No M^{II} compounds appear to have been isolated, but $[Ti(bipy)_2Br_2]Br$[85], $[V(chelate)_2X_2]X$[86] and $[V(chelate)_2X_2]$ $[V(chelate)X_4]$[86] are well-characterised. One of the vanadium compounds was assigned a *cis* configuration on the basis of its IR spectrum, but no unequivocal data are available on any of the compounds. The steric effect is expected to be large enough to preclude the existence of the *trans* isomer.

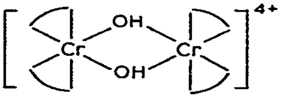
A variety of bis(chelate)vanadyl compounds $VO(chelate)_2X_2$(X = Cl, Br, ClO$_4$ and ½ SO$_4$) also have been reported[87], but no structural data.

(*iii*) *Chromium*

No bis(chelate)chromium(II) compounds appear to have been characterised, but good structural data are available on chromium(III) species.

Despite a variety of earlier assignments to the contrary, we have shown[11] that all data on the cations $[Cr(bipy)_2Cl_2]^+$ and $[Cr(phen)_2Cl_2]^+$ is best interpreted in terms of an invariable *cis* configuration. No evidence exists for the *trans* isomer. Anderson et al.[44] have reached the same conclusion on the basis of less extensive data, and have also considered the structure of other aniono-species.

An earlier report[88] of the *trans* as well as the *cis* isomers of the cations $[Cr(chelate)_2(H_2O)_2]^{3+}$ was soon retracted[89]. The species, which were assumed to be the *trans* isomers were shown[89] to be dimeric hydroxo- or oxo-bridged species. Recent kinetic data on the acid fission of the bridged species have been interpreted[90] as evidence for the μ-dihydroxo structure IV.



IV

(*iv*) *Manganese*

No manganese(III) compounds have been described, but they should be accessible.

The Mn-N distance in Mn^{II} compounds should be the longest in the complexes of the first-row transition series (Table 3). It is here, therefore, that the *trans* geometry should be looked for first. The only definitive data are on the compounds $[Mn(phen)_2(NCS)_2]$[57,81] and $[Mn(phen)_2I_2]$[81], which are *cis* octahedral (cf. Table 4). No structural data are available for the other known Mn^{II} compounds[65,81,91].

(*v*) *Iron*

The compounds $Fe(phen)_2X_2$ and $Fe(bipy)_2X_2$ have been widely studied, and are the subject of a recent review by Konig[82]. They are known in both high-spin and low-spin configurations and metal–chelate bond lengths are reported for both[59]. A rather long M-N distance (~ 2.2 Å) is known in the high-spin case, but there is no reliable evidence for the *trans* species in these compounds.

The structures of two examples of these compounds have been the subject of a number of papers.

Low-spin $[Fe(phen)_2(CN)_2]$ was first reported by Schilt[92]. Soon after Hamer and Orgel[93] assigned both this species and its protonated derivative $[Fe(phen)_2(CNH)_2]^{2+}$ a *cis*-octahedral configuration on the basis of the IR spectra of the solids. Then Schilt[67] reported the IR spectra of a variety of solvates of the compound, its Ru and Os analogues and similar bipyridyl species. Some of these compounds did not show the splitting into two bands of the C≡N stretching frequency, which is the basis of the assignment of the *cis* configuration. Therefore, although he believed the *cis* structure to predominate, Schilt[67] suggested that the *trans* isomer also was represented in his compounds. The Mössbauer evidence which he quoted to support this contention is not reproducible[68]. More recently, Schilt and Leman[94] reported analogous compounds with a variety of substituted phenanthrolines. Many of these also gave only one band in their IR spectra, and on this basis a *trans* structure was assigned. As noted in Section E, (iii) this is unreliable negative evidence, and not acceptable as *proof* of the *trans* structure, although the compounds may be worthy of further investigation. At least in solution in liquid HF, the cation $[Fe(phen)_2(CNH)_2]^{2+}$ has the *cis* configuration. There is good ^1H NMR and IR evidence for this[60].

The compound $[Fe(phen)_2(NCS)_2]$ is high-spin at room temperature[82]. An earlier IR study[83] found two bands near 2100 cm^{-1} and a structure $[\{Fe(phen)_2(NCS)\}_2](NCS)_2$ with bridging NCS was assigned. Species such as this have been characterised[7] for the nickel bipyridyl compound, and their IR spectra are very different from that of $Fe(phen)_2(NCS)_2$. The two bands in the C≡N region for the latter, separated by $\sim 10\ cm^{-1}$, were later more properly assigned to a *cis*-octahedral structure by Schilt and Fritsch[57]. Confirmation of the *cis* structure in the case of the bipyridyl species with very similar IR spectrum is now given by a full X-ray structural study[59].

Several mononuclear iron(III) species are known. Salts of the cation $[Fe(phen)_2Cl_2]^+$ were described by Harris and Lockyer[95], and those of $[Fe(chelate)_2(CN)_2]^+$ by Schilt[67]. No structural data are available, but the known Fe–N distances (Table 3) suggest that the *trans* isomer is unlikely to exist.

In addition, a variety of oxo- (or hydroxo-) bridged species, most of which appear to contain the cation $[\{Fe(chelate)_2\}_2O]^{4+}$, have been known for many years[96]. Details are given in two recent papers[97]. Many of the compounds may well have a five-coordinate structure as does an analogous salen compound[72].

(*vi*) *Cobalt*

A number of bis(chelate) cobalt(II) compounds have been characterised[57,81,84,91,98]. The green compound listed as $Co(phen)_2Cl_2 \cdot 2HCl$ by Pfeiffer et al.[91] is now known[18] to be $(phen\ H)_2[CoCl_4]$. Positive assignments of structure in this series are available only for the species listed in Table 4[81].

The cobalt(III) compounds have been the subject of many papers, especially by some Russian workers. In 1961, Ablov and Palade[99] reported that, unlike $[Co(en)_2(H_2O)_2]^{3+}$, the cation *cis*-$[Co(phen)_2(H_2O)_2]^{3+}$ did not isomerise to the *trans* isomer in water. Since then, they have reported many other species containing *cis* cations $[Co(chelate)_2X_2]^{n+}$, but throughout have been unable to find any evidence for a *trans* species. The most recent paper[100] reports a range of bipyridyl compounds *cis*-$[Co(bipy)_2X_2]X$.

It was Ablov et al.[45] who, in 1965, reported the X-ray crystal structure of the key compound α-*cis*-$[Co(phen)_2Cl_2]Cl \cdot 3\ H_2O$ (see section E, i); and in 1967 Palade[101] dealt with a previous report by Spacu et al.[102] that they had isolated *cis* and *trans*-$[Co(bipy)_2Cl_2]Cl$. One of the latter compounds was shown to be *cis*-$[Co(bipy)_2Cl_2]Cl$

and the other *cis*-$[Co(bipy)_2CO_3]Cl$. Quite recently Palade[15] has noticed the steric effect which apparently precludes the existence of the *trans* isomer.

The green compound, previously[103] supposed to be *trans*-$[Co(bipy)_2Cl_2]Cl$, was first shown by Aprile et al.[104] to give aqueous solutions which contained only *cis*-$[Co(bipy)_2Cl_2]^+$ and $[Co(bipy)_3]^{3+}$ cations, together with cobalt(II) species derived from $[CoCl_4]^{2-}$ in the solid. We[10] have confirmed these results, and have further shown the green materials prepared by such a method to be complex mixtures—probably mixed tertiary and quaternary phases. There is no evidence for the *trans*-$[Co(bipy)_2Cl_2]^+$ cation in them; although it is, of course, impossible to prove the non-existence of a *trans* isomer which might undergo facile reactions on dissolution of the material. The separation of $[CoCl_4]^{2-}$ salts is a recurrent problem in the preparation of cobalt(III) species[10,105].

Another very recent assignment of a green compound as the *trans* complex[61] also refers[10,62] to a compound of the type *cis*-$[Co(phen)_2Cl_2]_2[CoCl_4]$. We have prepared a variety of polymorphs and different crystalline species of such mixed cobalt(III)–cobalt(II) chloro compounds containing phenanthroline and bipyridyl, including the first reported isolation of salts of the $[CoCl_3(H_2O)]^-$ anion[10,18].

A green compound which Ablov[106] thought was *cis*-$[Co(phen)_2(H_2O)Cl]Cl_2$ has been shown instead to be simply *cis*-$[Co(phen)_2Cl_2]Cl \cdot xH_2O$ in different crystalline or almost amorphous forms[11].

Aprile et al.[107], in their recent paper on the hydrolysis of the *cis*-$[Co(bipy)_2(OAc)_2]^+$ cation, also have commented on the lack of any evidence for *trans* species.

The problem of the very different aquation rates reported by different authors for the cations *cis*-$[Co(chelate)_2Cl_2]^+$ has now been resolved by Josephsen et al.[108]. Cobalt(II) impurities catalyse the reactions.

The only outstanding problem in the assignment of structure to such cations is that of $[Co(chelate)_2(NO_2)_2]^+$. Lambert and Mason[109] prepared these cations by the method used for *trans*-$[Co(en)_2(NO_2)_2]^+$, and on this basis alone assigned the *trans* configuration to $[Co(phen)_2(NO_2)_2]^+$ and $[Co(bipy)_2(NO_2)_2]^+$. They did note that the phenanthroline compound appeared not to be different from that prepared by Ablov[106], and which had been assigned the *cis* configuration. Gomwalk and McAuley[110] have accepted the *trans* assignment, and think that one of the reactions they have observed in the acid hydrolysis of $[Co(phen)_2(NO_2)_2]^+$ can be assigned to a *trans* → *cis* change. Although there is no evidence to *prove* that these assignments of the *trans* structure are in error, there is equally no evidence for them. The two-stage acid hydrolysis[110] can be explained by other reaction schemes than the one they propose, and it seems best to assume the *cis* configuration until there is significant proof otherwise.

(*vii*) *Nickel*

Four coplanar low-spin $[Ni(chelate)_2]^{2+}$ species are not obtained; but the reason may be partly electronic, since we have not observed any low-spin $[NiN_4]^{2+}$ species with bis(2-picolylamine) compounds[18], and there is no steric effect here.

A wide variety of octahedral ions or molecules Ni(chelate)$_2$X$_2$ has been reported. In the most extensive series reported[7,111], we have assigned a *cis* configuration to all species, largely on the basis of the steric effect. More reliable data now are available from the electronic spectra of the compounds in the "near IR" region[27]. These are consistent with the *cis* configuration for all cases in which X is far enough from the chelate in the spectrochemical series (see Section E, ii). And in cases where this condition is not met, as in the N$_6$ chromophores with isothiocyanate[7,57] and isocyanate[112], the IR spectra of the anionic ligands usually provide acceptable information about structure.

These then become key compounds for assigning structures to other M(chelate)$_2$X$_2$ species on the basis of X-ray powder diffraction data (Table 4).

(*viii*) *Copper*

For the compounds Cu(chelate)$_2$X$_2$, [Cu(chelate)$_2$X]Y, and [Cu(chelate)$_2$R]Y$_2$ (where X = an anion; R = a unidentate neutral ligand; and Y = ClO$_4$, PF$_6$) a five-coordinate, essentially trigonal bipyramidal structure as in Fig. 7 has been assigned to the cations. This assignment was based on a great deal of physicochemical data[113], relating both to the solid state and solutions in non-aqueous solvents such as nitromethane and nitrobenzene; and was first proven in the case of [Cu(bipy)$_2$I]I by a full X-ray crystallographic study[2,114]. In addition, an incomplete study[115] of a crystal containing the cation [Cu(phen)$_2$H$_2$O]$^{2+}$ and disordered ClO$_4$$^-$ and PF$_6$$^-$ anions (for which latter the author admits responsibility) also shows essentially this geometry.

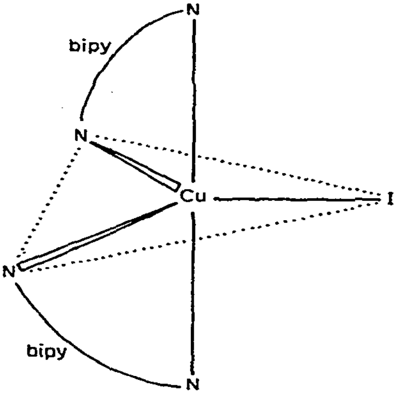


Fig. 7. The structure[2] of the cation in [Cu(bipy)$_2$I]I.

More recently, a crystal structure[31] of [Cu(bipy)$_2$NO$_2$]NO$_3$ has shown a grossly distorted *cis*-octahedral configuration for the cation, with a bidentate nitrite group. Largely on the basis of this structure (but also attempting to use the electronic spectra) Hathaway et al.[9] believe that the *cis*-octahedral geometry predominates in these series of Cu^{II} compounds. They are in error in their deductions. In our wider study[27,113,6] of the spectra of these compounds we have shown that the spectra do not fit at all nicely into the two classes desired by Hathaway et al. and most of the other data favours the five-coordinate geometry for most of these species. However, since in either geometry there is no problem of the steric effect, the argument will be pursued elsewhere. Both five-coordinate and six-coordinate *cis*-octahedral species exist in these series (an example of the latter is $[Cu(phen)_2(NCS)_2]$—see Table 4), but there is no sure way yet of defining which is the predominant geometry.

Of some interest are the compounds with anions which generally are reluctant to bond to the metal such as ClO_4^-, BF_4^- and PF_6^-. It is in these compounds, some of which are probably of the type $[Cu(chelate)_2]X_2$ (although ClO_4^- and BF_4^- coordination appears to occur in some cases[116]), that a planar array of the two chelates is most likely. However, a recent crystal structure[117] of $[Cu(bipyam)_2](ClO_4)_2$ shows an essentially tetrahedral geometry for the CuN_4 polyhedron. The angle between the chelate planes is ~ 60°. A similar geometry may occur in some of the phen and bipy compounds, but there is no way of proving this short of a full X-ray structural analysis. The electronic spectrum[118] of $[Cu(bipyam)_2](ClO_4)_2$ is not significantly different from that of a whole variety of tetragonal $[CuN_4X_2]$ and five-coordinate $[CuN_4X]^+$ chromophores[27]. In particular, the spectrum of $[Cu(phen)_2(H_2O)](ClO_4)_2$ (which is known to be five-coordinate[115]) is practically identical[27] with that of the dehydrated $[Cu(phen)_2](PF_6)_2$. On the other hand, there is a significant difference in the spectra of $Cu(bipy)_2(ClO_4)_2$ and $Cu(bipy)_2(PF_6)_2$, while that of the former is identical with that of $[Cu(bipy)_2ClO_4]PF_6$. The IR spectrum of $Cu(bipy)_2(ClO_4)_2$ in the Cl—O stretching region is the same as the sum of that of $[Cu(bipy)_2ClO_4]PF_6$ and a $[Cu(bipy)_2X]ClO_4$ species. Of these last two, the former has a broad flat-topped absorption band in this region—definitely showing a splitting of the Cl—O stretching frequencies, and the latter gives a sharp single band. Thus the two perchlorates in $Cu(bipy)_2(ClO_4)_2$ are in different sites in the crystal, and one of them may be involved in a bonding interaction with the copper cation in the solid. We have also reported the evidence for perchlorate bonding in nitrobenzene solution[116], and in the analogous Ni^{II} compounds[7,111]. Since this first report of perchlorate coordination in such cations, it has been firmly established for a variety of metal complexes[119].

Copper(II) species with a structure as in Fig. 6 may well exist, and these may be classified as *trans* if desired. Noack and Gordon[66] have interpreted the ESR spectra of a water-ethanol glass containing $Cu(bipy)_2(NO_3)_2$ as giving evidence of *cis* and *trans* isomers of the diaquo species. However, there is no evidence that even the *cis* diaquo species exists. This is an assumption made in the interpretation of the ^1H NMR data and is not proved by the latter (nor is it proved by the electronic spectra, or any other physicochemical data). The species normally present in water may well be five-coordinate $[Cu(bipy)_2H_2O]^{2+}$. The ESR data do give acceptable evidence for two species under the conditions of the measurement. These might be any two of the following: *cis*-$[Cu(bipy)_2(H_2O)_2]^{2+}$, $[Cu(bipy)_2H_2O]^{2+}$, "*trans*-$[Cu(bipy)_2(H_2O)_2]^{2+}$" (i.e., Fig. 5), $[Cu(bipy)_2NO_3]^+$, or species involving bonded ethanol.

The steric effect is probably, at least partly, responsible for the easy reduction[120] of these Cu^{II} species to the tetrahedral Cu^I cations.

(ix) *Zinc*

A few zinc compounds are known, but $[Zn(phen)_2(NCS)_2]$ is the only one for which any significant data are available. Its IR spectrum[57] in the C≡N stretching region characterises it as *cis*.

(x) *Gallium, indium and thallium*

A number of compounds containing the cations $[M(chelate)_2X_2]^+$ have been described.

Despite earlier assignments of the *trans* configuration to $[Ga(bipy)_2Cl_2]^+$ cations[121], at least one of them so assigned now has been shown[33] to be *cis*. There is no acceptable evidence that they are not all *cis*.

Indium(III) compounds have been described by Walton[122], who assigned a *cis* structure on the basis of IR and Raman data. The evidence is of course only circumstantial, but it fits with the expectation from the steric effects.

Both thallium(I) and thallium(III) compounds have been described[123]. Again relying on the far IR spectra, but in a most unsatisfactory manner, these authors assigned a *trans* configuration to the thallium(III) cations. They relied on the similarity of the spectrum of $[Tl(bipy)_2Cl_2]Cl$ to that of "*trans*-$[Co(bipy)_2Cl_2]Cl$"—but the latter is a complex mixture containing none of the *trans* cation[10] (see above). There is no evidence for structure in these thallium compounds, and X-ray evidence will be required for defining structure in these solids.

For the M^{III} species, the indium compounds are the most likely to give a *trans* isomer—having the longest M–N bond distance (probably ~ 2.2 Å by extrapolation from $[In\,Cl_5H_2O]^-$—Table 3). There will still be a steric effect, but it may be small enough to allow solid-state effects to stabilise the geometry.

(xi) *Molybdenum and tungsten*

Metal-nitrogen distances here can be as long as 2.4 Å (Table 3). Thus, if the softer model for the potential function for the non-bonded hydrogen interactions is applicable, the steric effect may be vanishingly small, and the *trans* geometry may occur.

The well-characterised species $[M(chelate)_2(CO)_2]$ have been assigned a *cis* configuration on the basis of their IR spectra[124] (CO stretching frequencies). A more recent study[125] includes measurements in solution in CS_2, so there is little doubt about the *cis* geometry in this solvent. A possible explanation of the "far IR" spectra of the solids is that they are a mixture of *cis* and *trans* isomers; but it is only a suggestion, and there is no real evidence for the *trans* isomer[125].

The only other species described are the compounds $Mo_2(bipy)_3X_6$ (X = Cl, Br)[126], which have been assigned the structure $[Mo(bipy)_2Cl_2]\,[Mo(bipy)Cl_4]$. No evidence is available for the configuration of the cation.

(xii) *Ruthenium and osmium*

A wide variety of compounds containing cations of the type $[M(chelate)_2X_2]^{n+}$, $[M(chelate)_2LX]^{(n+1)+}$ and $[M(chelate)_2L_2]^{(n+1)+}$ (where M = Ru, Os; X = an anion; L = a neutral ligand; and n = 1,0) has been described[3,5,127–129]. Mostly they have been assigned the *cis* configuration because of the steric effect[3,5,128]. However, it is interesting to speculate that, because these compounds are generally inert, they may well provide an example of a kinetically stabilised *trans* species. The best argument against this latter is the fact that they *are* so inert—especially to loss of a chelate—whereas the Pt^{II} and Pd^{II} compounds (q.v.) for which the *trans* geometry is known[14] are so labile.

(xiii) *Rhodium and iridium*

After a number of unhappy earlier assignments of configuration, based on prejudice rather than any concrete evidence, it now appears to be generally agreed[12,14,50,54] that the known cations $[Rh(phen)_2X_2]^+$ and $[Rh(bipy)_2X_2]^+$ all have the *cis* configuration. Three polymorphs of $[Rh(phen)_2Cl_2]Cl \cdot xH_2O$ have been characterised[12], one of which is isomorphous with α-*cis*-$[Co(phen)_2Cl_2]Cl \cdot 3H_2O$ of known[45] structure. A variety of synthetic procedures all produce this same inert *cis* cation, and there is no evidence for the *trans* isomer.

Rh^I compounds often are planar like the isoelectronic Pd^{II} compounds. Martin et al.[130] reported in 1961 several compounds apparently of the type $Rh(bipy)_2X$, to which they assigned a *trans* planar structure. However, no evidence which we could now accept for structure was presented. Doubts also have been raised about the basic nature of these materials.

A compound which was formulated[131] as *trans*-$[Ir(phen)_2Cl_2]Cl$, now has been shown[132] to be phenH$[Ir(phen)Cl_4]$. The inert cations $[Ir(chelate)_2X_2]^+$ all have been shown to have the *cis* configuration, since their compounds are isomorphous[50] with a known *cis*-Rh^{III} polymorph[12]. Further evidence for the *cis* configuration in the $[Ir(bipy)_2Cl_2]^+$ cation has been given by a recent ^1H NMR study[64].

(xiv) *Palladium and platinum*

Bis(chelate) compounds of these metals have been known since 1934, when Morgan and Burtsall[133] reported $Pt(bipy)_2Cl_2 \cdot 2H_2O$. The most extensive published study is that of Livingstone and Wheelahan[4], which includes $Pd(phen)_2X_2$, $Pd(bipy)_2X_2$ and $Pt(bipy)_2X_2$ compounds. It follows some earlier work by Livingstone[134].

There is a great wealth of chemical evidence to show the marked preference of these metals for the planar MN_4 geometry, although five-coordinate species are known with suitably bulky phosphine and arsine ligands. For these metals the steric effect is manifested chemically as a marked lability of one of the ligands[4,134–136], and structurally probably as a distortion of the ligands rather than the MN_4 polyhedron. At least in one case, the preliminary results of an X-ray study[14] of $[Pd(phen)_2](ClO_4)_2$ apparently show this. The ligands are said to be "bowed" about their C_2 axis. It will be interesting to learn by how much, if at all, the MN_4 polyhedron also is distorted.

A crystal structure of a palladium compound such as $Pd(chelate)_2I_2$ also may be of interest, since we cannot reject out-of-hand the possibility of a different coordination geometry, perhaps related to that[2] of $[Cu(bipy)_2I]I$. It will also be of interest to compare the distortions in bipyridyl with those in phenanthroline.

Platinum(IV) compounds also have been prepared[135], but there are no structural data available.

(*xv*) *Silver and gold*

A variety of bis(chelate) compounds of both silver(I) and silver(II) is well-characterised[137]. No structural data are available, but it is reasonable to expect the structures to be similar to those of the analogous copper compounds. Comparison of the X-ray powder patterns of the compounds of the two metals could well be useful here. In this connection, we note the preparation of mixed crystals of $Ag(phen)_2S_2O_8$ with its Cu and Cd analogues[137a].

The failure[141] to obtain bis(chelate) compounds of Au^{III}, which is isoelectronic with Pd^{II} and Pt^{II}, may be a result of the steric effect.

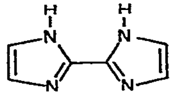
G. CONCLUSION

Thus, of the variety of claims for the *trans* structure in bisphenanthroline and bisbipyridyl metal compounds, the only cases for which acceptable evidence is available are with Pd^{II} and Pt^{II}; and this comes mainly from the results (albeit preliminary) of an X-ray structural determination[14], which fortifies our belief in the usual stereochemistry of these metals. Many of the claims in the literature for the *trans* species are either demonstrably wrong, or based on no acceptable evidence.

However, it is not to be concluded that *trans* species will not be found for other metals. In view of our lack of knowledge of the finer details of the steric effect in such compounds, and particularly the energy curves for the distortion of the metal polyhedra, it is premature to assume this.

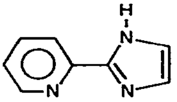
Of course, any further claims for a *trans* isomer will need to be based on firmer evidence than has often been accepted in the past; and in most cases this will mean a full X-ray structural study (unless the compound happens to crystallise in such a way that the metal lies on a crystallographic centre of symmetry).

In order to define more clearly the size of the non-bonded interactions in such metal complexes, it may be helpful to study similar ligands which have rather smaller steric effects. One approach is suggested by the known[138] *trans* geometry of the diaquobischelatenickel(II) cation of biimidazolyl (V). We calculate[18], from the published



V

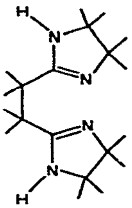
data, a non-bonded H-H distance of 2.46 Å, so there is no steric effect for the *trans* ligands. An intermediate ligand 2-imidazolyl-2-pyridyl (impy, VI) would give a non-bonded H-H distance of ~ 1.5 Å in an undistorted *trans,trans*-bis(impy) compound with an M-N distance of 2.0 Å[139]. This is a significant improvement on bipyridyl; and in this case small distortion of the ligand angles, each with little cost in energy, together with a twist about the C–C bond joining the two rings, may be sufficient to relieve the strain.


VI

It will be interesting to see if *trans* compounds of this and similar ligands[140] can be obtained, and if so to have accurate determinations of their geometry. Our preliminary study[139] of the chromium(III) and cobalt(III) complexes of VI shows that assignment of configuration from their electronic spectra is not satisfactory, because low-energy metal–ligand absorptions obscure much of the region of interest. So again it looks as though three-dimensional crystal structures will be required.

The inclusion of "bridging" atoms between the heterocyclic donor rings, as in 2,2'-dipyridylamine and the dipyrromethenes increases the steric problem in a planar arrangement of the chelates; but the added flexibility in the system allows this steric effect now to be overcome (cf. III). Substitution in the heterocyclic rings adjacent to the donor atoms will, of course, further increase the steric effect[142]. With two "bridging" atoms, as in the ligands VII and VIII, the flexibility of the chelates is such that *cis*-octahedral and *trans* arrangements of the two chelates in bis complexes is possible. The compounds $NiL_2(NCS)_2$ are *cis*-octahedral for ligand VIII and *trans*-octahedral for ligand VII. A *trans* planar complex $NiL_2(ClO_4)_2$ also is characterised for ligand VIII.

Analogous steric effects occur in a variety of other diamines, such as the methyl substituted derivatives of 2-picolylamine[144], and the quadridentate ligands IX which have terminal pyridyl groups[27,145].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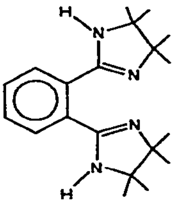
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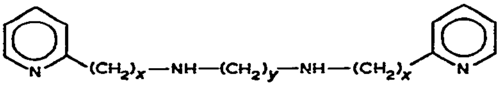
IX

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